# Book of Abstracts 2026
## (3rd Edition)

# PhD Day

23rd and 24th of April 2026,
Donostia- San Sebastian
Faculty of Chemistry

DIPC

EHU

POLYMAT

CIC biomaGUNE
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## WELCOMING & ACKNOWLEDGEMENTS

On behalf of the Organizing Committee, we are pleased to present the Book of Abstracts for the PhD Day 2026 (3rd Edition), held on the 23rd and 24th of April 2026. This volume compiles the contributions presented during the event and reflects the diversity and quality of research within our doctoral community.

This third edition introduced several updates, largely driven by the strong involvement of PhD candidates in the faculty. As a result, the program was expanded to include different presentation formats: Plenary Lectures, Oral Communications, and Flash Presentations. In this context, the event also featured an introductory industrial talk delivered by Palex Scientific. The poster session format from previous editions was maintained, once again gathering a significant number of contributions.

We would like to express our sincere gratitude to all contributors for their active participation, as well as to the attendees and listeners for their engagement and interest. The effort and dedication behind the organization of this event are also greatly appreciated, having been carried out with enthusiasm.

We now invite the reader to explore the Table of Contents and the following collection of abstracts.

### ORGANIZING COMMITTEE

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Jon Mattin Matxain Beraza (EHU, DIPC)

# ORAL & FLASH PRESENTATIONS

## Thursday, 23rd April

### Session 1 (9:15 - 11:00)

- **PL1:** *From academia to the industry* – Izasa Sciencific by Palex
- **OR1:** *Amphiphilic cyclic branched polyglycerol: synthesis and evaluation as drug carrier* – Eric Gómez
- **OR2:** *Preclinical Evaluation of the PET Radiotracer [18F]3F-4AP for in vivo Myelin Imaging* – Mariana Coimbra
- **OR3:** *Development of sialoglycomimetics for Siglec-based immune regulation* – Beatriz del Campo
- **PL2:** *Urease powered drug-loaded nanomotors for bladder cancer therapy* – Acsah Konuparamban

### Session 2 (11:30 - 13:00)

- **PL3:** *Fabrication of photocatalytic nanofibers by Green Electrospinning* – Mario Martínez
- **OR4:** *Similaritydriven -framework for data-efficient polymer property prediction* – Amaia Elizaran
- **OR5:** *Predictive Rheology for Tailoring the Mechanical Behavior of PBSA/PLA MFCS* – Johan Garcia
- **OR6:** *New Generation of Tetraphenylborate-based Photobase Generators for Additive Manufacturing* – Oihane Varela
- **OR7:** *Fluorine-free coating made by seeded semibatch polymerization* – Pablo Morales

### Session 3 (15:30 - 16:30)

- **PL4:** *Synthesis of Planar Chiral [2.2] Paracyclophanes via Biocatalyzed Desymmetrization of Primary Alcohols* – Daniel Alonso
- **OR8:** *Photodriven ion transport through an Organic Mixed Ionic Electronic Conductor (OMIEC): Towards light gated ion pumps* – Martin Trapero
- **OR9:** *Redox Activation of Ru-Flavin Complexes* – Nitin Kumar

## Friday, 24th April

### Session 5 (10:15 - 11:10)

- **OR10:** *Structure-Function Relationships in Electro catalytic Systems: A surface science approach* – Sruthibhai Palakkattu
- **FP1:** *Towards the discovery of the receptor of (+)-Conagenin* – Ioritz Arburua

- **FP2:** *Hybrid Electrolytes Optimization by Rheology-Guided Extrusion for Solid-State Lithium Batteries* – Iker Varona
- **FP3:** *Mechanistic Insights into Transfer-Dominated Branching Radical Telomerization through Kinetic Monte Carlo Simulation* – Oihan Lamarins
- **FP4:** *Enhancing processability of PLA/PBSA blends for packaging applications* – Iosu Burgaña
- **FP5:** *Interpenetrating Gel Polymer Electrolytes: Effects of PEO Structural Design* – Valentina Colli
- **FP6:** *New Synthesis Pathways Of Sustainable Polyurethanes With Barrier Properties* – Akshaya Maria
- **FP7:** *Designing (de) bonding chemistries in coatings and adhesives for recycling of the substrates* – Amirhossein Enayati
- **FP8:** *Late-Stage C-H Sulfonylation of Simple Phenols and Phenol-Containing Biomolecules* – Martin Villamor

**Session 6 (11:45 - 12:40)**

- **OR11:** *Extensional and microrheological characterization of HA solutions for 3D printing processing* – Itziar Insua
- **FP9:** *Molecular Pathways of LCST and UCST Behavior in Ionic Liquid water mixture* – Hussen Oumer
- **FP10:** *Deconstructing a-Aminoalkyl Sulfones as Dual d-Sulfonyl/ a-Azomethine Synthons: Synthesis of 3-Sulfonylmethylindole Aminals* – Anje Mujika
- **FP11:** *SET-driven radical formation in nitroaromatics* – Lisa Ebo
- **FP12:** *Anionic Ring-Opening Polymerization of Cyclic Carbamates* – Irati Celada
- **FP13:** *Voltage-Dependent Hydrogen Evolution on PtGe Surfaces* – Idoia Camara
- **FP14:** *DNA-based Catalysis Membrane Reactor* – Helia Ventribout
- **FP15:** *Co-Catalyzed Intramolecular C-H Alkylamination of Tyrosine Derivatives* – Nerea Cirauqui
- **FP16:** *Advanced Surface Modification for Automotive Polymer Adhesion* – Asier De Santos

## POSTER PRESENTATIONS

*(Sorted in alphabetical order by presenter's last name)*

- *Assessment of filamentous fungi with dye-degrading potential isolated from basque estuaries* – Agirrezabala Urkia, Ziortza
- *Sustainable and chemically recyclable ppef nanocomposites for advanced packaging applications* – Alam, Md Shafi
- *Solid lipid nanoparticles: innovative tools against resistant bacteria* – Altube Urquia, Oihane
- *Development of waterborne paints as passive daytime radiative cooling (pdrc) materials* – Aramberri, Janire
- *Mechanistic studies of copper (i)-catalyzed enantioselective cross aldol reactions of a-ketoamides* – Artieda Rota, Jon
- *Enhanced lithium-ion conductivity in glassy chloride solid electrolytes* – Azabal Martin, Claudia
- *Anti-selective cross-aldol reactions of schiff bases of glycine o-nitroanilide and applications in peptide synthesis* – Campo, Maria
- *Engineered proteins-nanocluster hybrid nanotools for combination therapies against cancer* – Carpintero Cueto, Eva
- *Adhesion of conducting polymer electrodes for implantable devices* – Cid, Andrea
- *Morphology, crystallization and thermal properties of biodegradable and double crystalline poly(7-hydroxybutyrate)-b-poly(lactide) diblock copolymers* – Cimino, Arianna Teresa
- *Studying the organization of collagen fibers in engineered bioprinted materials using shg-microscopy and saxs* – de Oliveira, Guilherme Henrique
- *The next level of sustainability in emulsion polymerization* – de Oliveira Lima, Luana Caroline
- *Synthesis of biodegradable copolyesters from monomers that can be derived from biomass: characterization and application* – Elorza, Marta
- *Desymmetrization of [2,2]paracyclophanes via the wittig reaction* – Fernández Pascual, Héctor Elpidio
- *Abs material properties: influence of thermal and mechanical aging* – Ferrer Diaz, Beatriz
- *Exploration of chiral anionic organobases as catalysts for enantioselective synthesis of chiral y-nitrosulfones* – Ferreras Martinez, Iker

- *Synthesis of new molecular entities based on glycomimetics* – Fuertes Cayón, Nerea
- *Mixed ionic electronic conducting polymers based on pedot:pss and protic organic ionic plastic crystals* – García Foronda, Paula
- *Strategies towards the late-stage bioconjugation of tyr-containing peptides* – Girón Elola, Carlota
- *The influence of composition and coupling approaches on g-c3n4/pedot:pss hybrid thin films* – Guerra Mantzizidor, Maialen
- *Balancing adhesion and cohesion in high bio-content itaconate-based waterborne pressure-sensitive adhesives reinforced with cellulose nanocrystals* – Gupta, Jyoti
- *Ynone-promoted coupling of nitromethane to gramines* – Gurrutxaga Cardenal, Iker
- *Single chain nanoparticles for applications in nanomedicine* – Gutiérrez Lkourt, Sara
- *Delivery and activation of organometallic anticancer drugs using ionic liquids* – Hernández Fernández, Laura
- *Dry & wet processed gel-polymer electrolytes and cathodes* – Imaz Elizalde, Paul
- *Development of semicrystalline sustainable polymers* – Jagtap, Chetan
- *Unseen forces: the overlooked role of flow conditions in polyelectrolyte multilayer formation and their impact on membrane pore modification* – Kogal, Kaja
- *Innovative techniques to process polymer latexes: 3d printing* – Larrañaga Medinilla, Jon
- *Bio-based polymer electrolytes for li metal batteries* – Larumbe, Mikel
- *Integrating molecular dynamics and ml for predictive modeling of ipps* – Lobato Basterra, Héctor
- *Designing poly (butylene succinate)/poly (butylene adipate-co-terephtalate)/poly (lactic acid) blends for material extrusion additive manufacturing* – López Matanza, Pablo
- *Morphology driven performance improvement of waterborne pressure-sensitive adhesives* – Malter, Marc Frederic
- *Nipu/epoxy hybrid polymers based on carbonated soybean oil (csbo): the influence of covalent adaptable networks (can) on reprocessability* – Martin Larrañaga, Nahikari

- *3d printing of responsive biomaterials for bacterial infection sensing* – Muñoz Mateo, Ana María
- *Synthesis of quantum dots based on novel materials for single photon light-sources* – Murkina, Anastasiia
- *Understanding and improving substrate adhesion of polymer dispersions* – Negaresh, Mohammadmahdi
- *Cofactor loaded enzyme-polymer hybrids* – Ontoria, Aitor
- *Pd-catalyzed c(sp²)-n directed amidations of tyrosine-containing peptides* – Pérez Cubero, Iván
- *Oragnocatalyzed polyacetal formation using catalytic acid:base complexes* – Pinheiro, Gabriela
- *Waterborne polymer dispersion crosslinked by the thiol-epoxy reaction* – Rodriguez Mugica, Iker
- *Synthesis and characterization of poly(4-vinylpyridine) functionalized membranes* – Roldan Rosas, Unax
- *Novel approaches to flavin-like photochemistry on earth-abundant metal substrates* – Rotundo, Alfredo Manuel
- *Miniemulsion polymerization of cardanol methacrylate for high biobased content coatings* – Rubio, Sara
- *Taylor-made blends of polyhydroxyalkanoates with improved mechanical properties and processing behaviour* – Salsé Rosera, Pilar
- *Developing a novel liquid wound dressing to treat the superficial wounds* – Sanjarnia, Pegah
- *Chaotic printing as a strategy for enzyme immobilization* – Sansiñena Emazabel, Gorane
- *Investigation of the effect of carbon dots on the crystallization kinetics and thermal behavior of poly(e-caprolactone)* – Shariatikia, Fateme
- *Hydrophobicity gradients control function in short peptide self-assembled nanostructures* – Toledo Alday, Irene
- *Impact of aliphatic glycol chain length in polycaprolactone based random copolyesters* – Torres Rodríguez, Juan
- *Protective superhydrophobic coating for ceramic substrate* – Xin, Yuanyuan
- *Synchrotron x-ray radiation to study cellular reactivity of metal complexes* – Zingales, Esteban

# Amphiphilic cyclic branched polyglycerol: synthesis and evaluation as drug carrier

Eric Gómez Urreizti, Fabienne Barroso-Bujans

*Student Name:* Eric Gómez Urreizti
*PhD programme: Física de nanoestructuras y materiales avanzados*
*Laboratory Group Name: Polymers and Soft Matter Group (PSMG)*
*Year of enrolment:  3rd Year and more*

The development of unimolecular nanocarriers is essential to overcome the inherent instability of micellar aggregates. While $B(C_6F_5)_3$-catalyzed glycidol (Gly) polymerization is well-documented, its copolymerization with cyclohexene oxide (CHO) remains unexplored. This study investigates the synthesis and characterization of cyclic-branched copolymers with varying CHO:Gly ratios via zwitterionic ring-opening polymerization. MALDI-TOF MS confirmed exclusively cyclic architectures, while in-situ $^1$H-NMR kinetic studies revealed similar monomer consumption rates, supporting a statistical distribution. Glass transition temperatures ($T_g$) showed excellent agreement with the Fox equation ($R^2$=0.96), demonstrating predictable thermal behavior. To create amphiphilic carriers, p(CHO-st-Gly)$_{90-10}$ was used as a macroinitiator for glycidol hyperbranching, yielding hbPG-g-p(CHO-st-Gly)$_{90-10}$. This core-shell architecture significantly improved water solubility and achieved a 500% increase in curcumin uptake compared to a hydrophilic control. Sustained release was observed, reaching a plateau of 48% over seven days. Biological evaluation in hCMEC/D3 cells confirmed the system's biocompatibility via MTT assays. Furthermore, the nanocarriers successfully crossed an in vitro blood-brain barrier (BBB) model with a permeability coefficient of $7.2 \times 10^{-5}$ cm/min. Preliminary results indicate that the controlled release of curcumin effectively inhibits β-amyloid ($\beta A_{1-40}$) aggregation. These findings establish cyclic-branched architectures as a promising unimolecular platform for the stable and brain-permeable delivery of hydrophobic drugs.

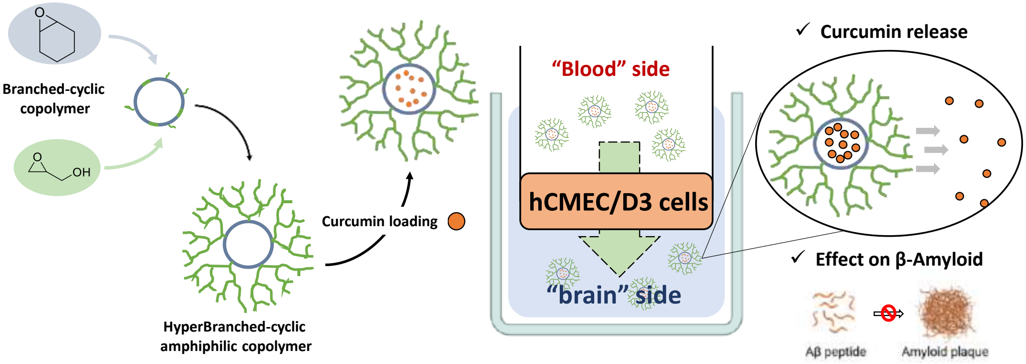

***Figure 1.*** Schematic representation of the cyclic-branched unimolecular nanocarrier platform for brain-targeted curcumin delivery.

**Keywords:** Drug release, curcumin, copolymer, polyglycidol, amphiphilic.

## References

[1] J. Public, A. Nonymous, *Journal Name*, Year, *Volume*, page.

[2] A. Nonymous, J. Public, *Journal Name*, Year, Issue, page.

# Preclinical Evaluation of the PET Radiotracer [$^{18}$F]3F-4AP for in vivo Myelin Imaging

Mariana M. Coimbra de Almeida[1], Claudia Espósito Zapero[1], Pedro Brugarolas[2], Vanessa G. Vallejo[1], Pedro R. Cabrer[1], Jordi L. Roig[1]
[1]CICbiomaGune, Radiochemistry and Nuclear Imaging, San Sebastián, Spain
[2]Massachusetts General Hospital and Harvard Medical School, Radiology, Boston, United States of America

*Student Name: Mariana Matos Coimbra de Almeida*
*PhD programme: Synthetic and Industrial Chemistry*
*Laboratory Group Name: Radiochemistry and Nuclear Imaging*
*Year of enrolment:* ☐ *1st Year* ☐ *2nd Year* ☒ *3rd Year and more*

Alzheimer's disease (AD) is a neurodegenerative disorder predominantly characterized by amyloid-β deposition, tau pathology, synaptic dysfunction, and neuroinflammation. Nevertheless, recent evidence highlights myelin degeneration as another early pathological event, underscoring myelin preservation and repair as a potential therapeutic strategy. To enable non-invasive monitoring of myelin status, [18F]3F-4AP, a positron emission tomography (PET) radioligand that targets potassium channels exposed during demyelination, was synthesized and evaluated in vivo in two different animal models.

Female C57BL/6 mice underwent longitudinal cuprizone-induced de- and remyelination, with PET and T2-weighted MRI acquired at baseline, peak demyelination, and during recovery. Second, a cross-sectional study was conducted in 9-month-old female 5xFAD mice and wild-type controls to assess tracer sensitivity in an amyloid-driven model. Tracer uptake and non-displaceable binding potential (BPND) were quantified in highly myelinated brain regions.

MRI confirmed partial demyelination and subsequent recovery in the cuprizone model. While global PET uptake showed no significant changes, a trend toward increased BPND was observed in white matter and striatum during demyelination.

In contrast, 5xFAD mice exhibited significantly higher [$^{18}$F]3F-4AP BPND compared to controls across multiple myelinated regions (Figure 1), indicating enhanced sensitivity in the Alzheimer mouse model.

These results highlight [$^{18}$F]3F-4AP as a promising PET biomarker for detecting myelin alterations in Alzheimer's disease. Ongoing studies will expand quantitative analyses in the 5xFAD and a sporadic AD model, and assess its ability to monitor remyelination therapies, supporting its translational utility for tracking disease progression and treatment response.

**Keywords:** Alzheimer; Cuprizone; Demyelination; PET; MRI

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# Development of sialoglycomimetics for Siglec-based immune regulation

Beatriz del Campo,[1,2] Niels. C Reichardt,[1] June Ereño [2]

*Student Name: Beatriz del Campo Herrero*
*PhD programme: Química Sintética e Industrial*
*Laboratory Group Name: Glycotechnology Laboratory (CICbiomaGUNE)*
*Year of enrolment: ☐ 1st Year ☐ 2nd Year* ***3rd Year and more***

Cell surfaces are coated with a complex layer of glycans known as the glycocalyx [1]. This structure is enriched in sialic acid–containing glycans, which play a critical role in immune regulation, inflammatory processes, and the progression of certain cancers [2]. These terminally sialylated structures are specifically recognized by Siglecs (sialic acid–binding immunoglobulin-like lectins), a family of I-type lectin receptors predominantly expressed on immune cells. Upon interaction, molecular and cellular responses that are essential to the function of the cells expressing Siglecs are triggered. Consequently, Siglecs are considered promising therapeutic targets for several diseases. However, despite their biological importance, understanding how Siglecs interact with glycans remains challenging due to the complexity and conformational flexibility of carbohydrate molecules.

Given that gangliosides serve as natural ligands for Siglecs [3], this project focuses on the design and synthesis of novel glycomimetics derived from the ganglioside **1** scaffold that allows multiple sites for structural modification to optimize affinity and specificity. Binding affinity and selectivity will first be assessed using microarray assays. The most promising candidates will then undergo detailed competitive Saturation Transfer Difference Nuclear Magnetic Resonance (STD-NMR) studies to identify critical ligand–protein interaction epitopes. The structural and interaction insights obtained will guide the rational design of glycomimetics with improved Siglec binding and modulatory potential. Ultimately, this methodology aims to provide lead compounds that could serve as foundational scaffolds for the development of next-generation glycan-based immunotherapies, contributing to targeted immune modulation in diverse pathological contexts.

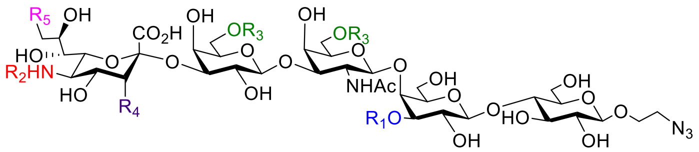

***Figure 1.** Structure of ganglioside **1**.*

**Keywords:** Sialoglycomimetics, Siglecs, Sialic acid, Immune system.

**References**

[1] van den Berg. B. M; Vink H; Spaan J. A. *Circulation research*, **2003**, *92*, 592-594.

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# Urease powered drug-loaded nanomotors for bladder cancer therapy

Acsah Konuparamban[1,2], Inés Macias Tarrio[3], Kristin Fichna[3], Jordi Llop[1], Samuel Sanchez[3]
[1]Center for Cooperative Research in Biomaterials (CIC biomaGUNE), Basque Research and Technology Alliance (BRTA).
[2]Euskal Herriko Unibertsitatea (UPV/EHU), 20018 Donostia, Spain
[3]Institute for Bioengineering of Catalonia

Student Name: Acsah Konuparamban
PhD programme: Synthetic and Industrial Chemistry
Laboratory Group Name: Radiochemistry and Nuclear Imaging
Year of enrolment: ☐ 1st Year ☐ 2nd Year ■ 3rd Year and more

Bladder cancer is the ninth most common cancer worldwide and remains challenging to treat due to high recurrence rates and limited efficacy of current therapies. To improve drug delivery within the bladder, we developed urease-powered nanomotors designed to actively enhance drug distribution and tumor targeting. In this work, drug-loaded nanomotors based on polymeric and mesoporous nanoparticle platforms were developed and evaluated for bladder cancer therapy in orthotopic murine models. In vivo therapeutic efficacy was assessed using Magnetic Resonance Imaging (MRI) to monitor tumor progression and response to treatment. Nanomotor-treated animals demonstrated significant tumor regression compared with untreated controls. In one study, the Mitomycin C loaded mesoporous silica nanobots (MsNM-MMC) reduced tumor volumes from 14.8 ± 8.6 mm³ to 9.9 ± 17.9 mm³, corresponding to a tumor fold change of 0.49 ± 0.65, indicating a strong therapeutic response. In a second orthotopic model using drug-loaded PLGA nanomotors, five out of six treated mice showed tumor regression, with the most responsive animal exhibiting a tumor reduction of 98.41%. Survival analysis demonstrated therapeutic benefit. Control mice showed rapid tumor progression with a median survival of 22 days, whereas nanomotor-treated mice showed significantly prolonged survival, with 50% remaining alive beyond 40 days. Overall, these findings demonstrate that urease-powered nanomotors can enhance local drug delivery and significantly improve therapeutic outcomes in bladder cancer, highlighting the potential of active nanomedicine approaches for future localized cancer therapies.

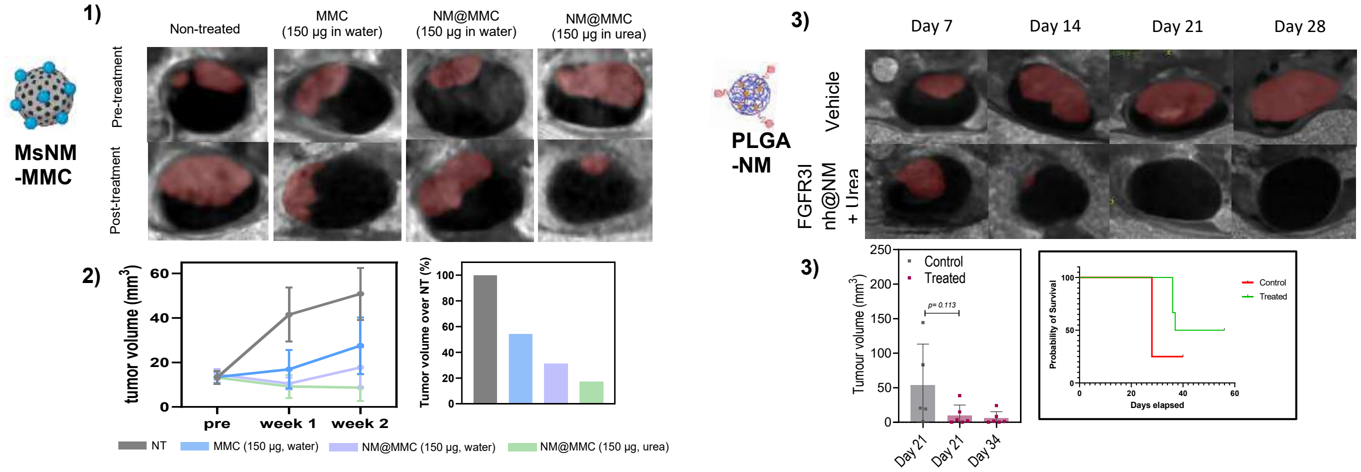

***Figure.*** *1) Diffusion weighted MRI scans showing bladder images pre- and post- treatment of control and treated mice with MsNM-MMC, 2) Graphs showing tumour volume change before and after therapy with MsNM-MMC. 3) Diffusion weighted MRI scans showing treatment bladder images of control and treated mice with PLGA-NM upto 4 weeks, 4) Graphs showing tumour volume change before and after therapy with PLGA-NM and Survival graph of control and treated groups.*

**Keywords:** Nanomedicine, Bladder cancer, oncolog

**References:** [1] Bray, F (2024). Global cancer statistics 2022 *CA: A Cancer Journal for Clinicians, 74*(3), 229–263. [2] Patiño Padial, T (2025). Swarming intelligence in self-propelled micromotors and nanomotors. *Nature Reviews Materials, 10*(12), 947–963.

# Fabrication of photocatalytic nanofibers by Green Electrospinning

Mario Martinez Yubero, Edurne González Gandara

*Student Name: Mario Martinez Yubero*
*PhD programme: Applied Chemistry and Polymeric Materials*
*Laboratory Group Name: GIQ*
*Year of enrolment: ☐ 1st Year ☐ 2nd Year X 3rd Year and more*

Green Electrospinning was employed to fabricate photocatalytic nanofibers designed for environmental remediation. To this end, methyl methacrylate/n-butyl acrylate (MMA/BA) copolymer particles stabilized with ultrafine titanium dioxide nanoparticles ($TiO_2$ NPs) were synthesized via miniemulsion polymerization.[1] Two latexes with a solids content of 40 wt % were prepared, containing 10 and 20 wt % $TiO_2$ NPs (based on monomers). These latexes were successfully electrospun using polyvinyl alcohol (PVA) as a template polymer, with a minimum PVA concentration of 30 wt % required to obtain continuous nanofibers. The resulting fibers contained only 3 and 6 wt % $TiO_2$ NPs . Since $TiO_2$ NPs were strongly adsorbed onto the polymer particle´s surface, an excellent distribution of the NPs along the nanofibers (without any aggregation) was guaranteed. The hybrid nanofibers were subsequently crosslinked to enhance their water stability. Their photocatalytic performance was evaluated through methylene blue (MB) degradation and *Escherichia coli* (*E. coli*) inactivation tests.[1,2] In both cases, the nanofibers exhibited significantly higher activity than corresponding films, attributable to their much larger surface area to volume ratio. Additionally, increasing the $TiO_2$ NPs content improved both MB degradation and bacterial inactivation efficiency. Moreover, the nanofibers demonstrated good reusability. Overall, this work highlights the potential of Green Electrospinning as a solvent-free approach to produce highly photocatalytic nanofibers capable of removing organic pollutants and pathogenic bacteria from water.

**Keywords:** Photocatalytic $TiO_2$, nanofibers, electrospinning, Pickering-stabilized latexes, antibacterial properties.

## References

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# Similarity-driven framework for data-efficient polymer property prediction

Amaia Elizaran Mendarte, Gustavo A. Schwartz

*Student Name: Amaia Elizaran Mendarte*
*PhD programme: Physics of Nanostructures and Advanced Materials*
*Laboratory Group Name: Polymers and Soft Matter Group – CFM (Centro de Física de Materiales)*
*Year of enrolment: ☐ 1st Year ☒ 2nd Year ☐ 3rd Year and more*

Prediction of polymer properties is crucial in designing new, advanced materials. In recent years, artificial neural networks (ANNs) have become increasingly popular for quantitative structure-property relationship (QSPR), which enables property prediction directly from polymers' structures. However, data scarcity significantly affects the applicability of these models and still remains a major limitation in the field [1]. Here, we present a data-efficient method to tackle data scarcity and enhance performance of an ANN in predicting glass transition temperature ($T_g$). We extended the similarity principle [2], which states that molecules with similar structures are expected to exhibit similar properties, to develop two similarity-driven frameworks for data-efficient few-shot polymer property prediction [3]. On the one hand, the chemical similarity method, which incorporates SMILES representations and $T_g$ values, enables a mean absolute percentage error (MAPE) of 7.8% using as few as 5 to 10 molecules for training. On the other hand, the structural similarity method, based only on SMILES-encoded polymer structures, without any physical property information, achieves a MAPE of the order of 15% using only 15 to 25 samples. These findings demonstrate that the proposed data-efficient strategy for addressing data scarcity provides accurate predictions of polymers' $T_g$, outperforming conventional ANN approaches used for QSPR applications.

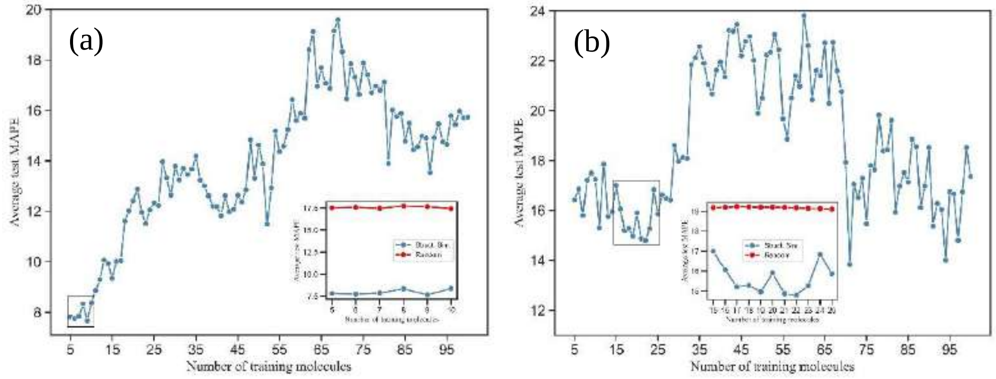

***Figure 1.*** *MAPE of test molecules depending on the number of training samples. The zoomed region shows the comparison between the method and employing random training samples. (a) Chemical similarity method results. (b) Structural similarity method results.*

**Keywords:** data scarcity, artificial neural networks, SMILES, molecular similarity

## References

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[2] A. Bender, R.C. Glen, *Org. Biomol. Chem.*, 2004, 2, 3204-3218. https://doi.org/10.1039/B409813G
[3] Y. Chen, et al., *J. Mater. Chem. A.*, 2024, 12, 30249-30268. https://doi.org/10.1039/D4TA06452F

# Predictive Rheology for Tailoring the Mechanical Behavior of PBSA/PLA MFCs

Johan Garcia, Itxaso Calafel, Itziar Otaegi, Gonzalo Guerrica-echavarria, Nora Aranburu

*Student Name: JOHAN ESTEBAN GARCIA PUENTES*
*PhD programme: PhD in Applied Chemistry and Polymeric Materials*
*Laboratory Group Name: Polymer Technology*
*Year of enrolment: □ 1st Year x 2nd Year □ 3rd Year and more*

Amid the growing demand for biodegradable polymers rivaling petroleum-based performance, poly(butylene succinate-co-adipate) (PBSA)/poly(lactic acid) (PLA) blends have emerged as a promising alternative. These bio-based systems integrate PBSA's ductility and flexibility with PLA's stiffness and barrier properties. Additionally, PBSA/PLA (70/30) blends enable in situ microfibrillar composites (MFCs), where dispersed PLA droplets transform into oriented fibrils during twin-screw extrusion followed by cold drawing [1]. This morphology enhances the reinforcing efficiency of the dispersed phase, improving mechanical performance and barrier properties. In this context, the present study employs rheological analysis as a predictive tool for microfibril formation under specific conditions. The effect of viscosity and elasticity ratios was evaluated through viscoelastic and shear rate responses, correlating parameters such as temperature, screw speed, and phase selection [2,3]. The experimental results were validated by processing PBSA/PLA MFCs at different draw ratios (DR). Tensile testing showed maximum strength and modulus at DR 5.0–6.5, consistent with dynamic rheology indicating higher storage modulus (G′) from fibrillar reinforcement. DMTA revealed an upward shift in PLA's $T_g$ due to restricted chain mobility, while DSC confirmed an increase in PLA's melting temperature ($T_m$) and crystallinity resulting from heterogeneous nucleation. SEM (see figure 1) validated the progressive development of fibril aspect ratio and thickness, confirming efficient stress transfer and interphase adhesion within the composite matrix.

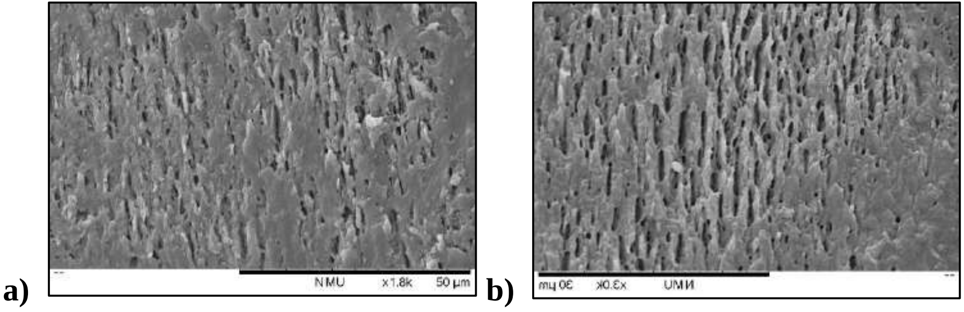

***Figure 1.*** *SEM micrographs of the PBSA/PLA blends at DR 1.2 (a) and DR 2.8 (b), showing the microfibrillar morphology with the aligned microfibrillar structure after selective dissolution of the dispersed phase in 20 wt% NaOH.*

**Keywords:** PBSA; PLA; microfibrillar composites (MFC); rheological analysis; biodegradable blends; thermal properties; mechanical reinforcement.

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# New Generation of Tetraphenylborate-based Photobase Generators for Additive Manufacturing

Oihane Varela Manrique, Xabier Lopez de Pariza, Haritz Sardon

*Student Name: Oihane Varela Manrique*
*PhD programme: Applied Chemistry and Polymeric Materials*
*Laboratory Group Name: Sardon Lab*
*Year of enrolment:* ☐ *1st Year* ☐ *2nd Year* ☒ *3rd Year and more*

Photobase generators (PBGs) are light-activated compounds that initiate polymerization by releasing organic bases upon irradiation. Their ability to activate base-catalyzed reactions with high spatial and temporal control makes them promising candidates for advanced 3D printing technologies However, their use in digital light processing (DLP) remains limited due to their lower efficiency compared to radical photoinitiators, as well as the inherently slower kinetics of many anionic polymerization processes. In addition, most reported PBGs require high-energy UV light for activation, which is not compatible with the wavelengths typically used in commercial DLP printers. To overcome this limitation, photosensitizers are often required to shift PBG activity to the longer wavelengths used in DLP printers, which introduces additional energy-transfer steps, reduces polymerization rates, and compromises resin stability.

In this work, we report the development of an anthraquinone-based unimolecular PBG integrated into a polythiourethane resin system. This design allows direct light absorption at DLP-compatible wavelengths, eliminating the need for an external photosensitizer while improving polymerization speed and resin stability, enabling efficient enabling efficient application in vat photopolymerization processes. Additionally, the polythiourethane network employed here has been previously demonstrated to be chemically recyclable, making it a suitable platform for the development of sustainable photopolymerizable resins. [1]

Overall, this study demonstrates a viable strategy to expand the use of PBGs in DLP-based 3D printing, providing an alternative to radical photoinitiators and opening new opportunities for the development of potentially recyclable and degradable materials.

**Keywords:** polymers, photopolymerization, 3D printing

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# Fluorine-free coating made by seeded semibatch polymerization

Pablo Morales, Aitor Barquero, Miren Aguirre

POLYMAT, Kimika Aplikatua Saila, Kimika Fakultatea, Euskal Herriko Unibertsitatea, UPV/EHU, Joxe Mari Korta Zentroa, Tolosa Hiribidea 72, 20018 Donostia/San Sebastián, Spain

*Student Name: Pablo Morales Cardador*
*PhD programme: Applied Chemistry and Polymers*
*Laboratory Group Name: Polymat, Polymerization Processes*
*Year of enrolment: ☐ 1st Year X 2nd Year ☐ 3rd Year and more*

Polymeric coatings for fabrics are essential to obtain water and oil repellent clothes. For textile applications, fluoropolymers have been dominating the market thanks to their excellent properties. However, as fluorinated compounds release harmful and long-lasting chemicals to the environment, world-wide agencies have imposed new regulatory restrictions on their use. As a result, fluor-free hydrophobic polymers have emerged as an alternative, and with the use of emulsion polymerization technique, VOC-free hydrophobic coatings can be synthesized.

As textile fibers are mainly negatively charged, in this project, cationically stabilized latexes have been produced, using the hydrophobic monomer stearyl methacrylate. Due to its hydrophobic character, the polymerizations faced low monomer solubility and low monomer mass-transfer[1]. In order to overcome these challenges, a low CMC surfactant[2], a catalytic phase transfer agent and an organic cosolvent[3] were added in the formulation.

In this work, these combined strategies have been used to achieve high conversions and low coagulum latexes using semibatch emulsion polymerization. It was concluded that the use of a hydrophilic seed resulted in higher conversions, as the need of a nucleation step was avoided. The efficiency of the phase transfer agent was improved by lowering the feeding rate of the pre-emulsion and also by controlling the initiator feeding strategy to obtain high instantaneous conversions throughout the reactions. The wettability properties of the polymer films resulted in a high-water contact angle and low water uptake, proving the hydrophobic properties of the coating.

**Keywords:** Waterborne coatings, Cationic emulsion, Hydrophobic materials.

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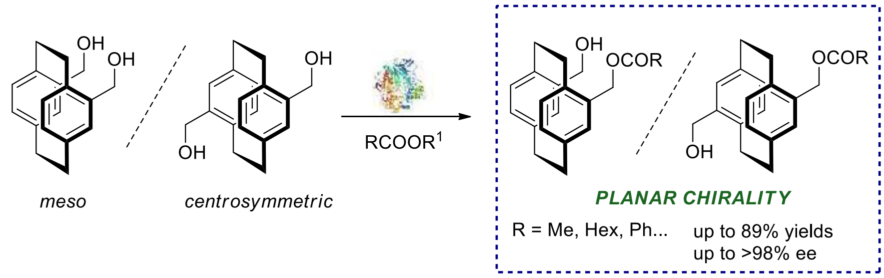
# Synthesis of Planar Chiral [2.2]Paracyclophanes via Biocatalyzed Desymmetrization of Primary Alcohols

Daniel Alonso, Nahia Egaña, Enrique Gómez Bengoa, Rosa López

*Student Name: Daniel Alonso Diez*
*PhD programme: Synthetic and Industrial Chemistry*
*Laboratory Group Name: Dep. Organic Chemistry I*
*Year of enrolment: 3rd Year*

Recently, considerable research efforts have been devoted to chiral backbones based on rigid and conformationally stable [2.2]paracyclophanes (PCPs), as they have emerged as highly promising chiral ligands for asymmetric catalysis and related fields.[1] The unique physical and chemical properties of PCPs further expand their utility as π-stacked conjugated polymers, hole-transport materials, … among others. From a synthetic point, substantial progress has been made in the selective functionalization of defined positions on the PCP scaffold. Nevertheless, achieving stereoselective control remains a major challenge, since access to enantiopure PCPs still largely relies on chromatographic resolution techniques.[2] To address this limitation and advance the preparation of enantiopure [2.2]PCPs, we have focused on catalytic carbon–heteroatom bond-forming strategies that enable the efficient differentiation of enantiotopic groups in meso and centrosymmetric disubstituted PCPs. Herein, we report a biocatalytic transesterification protocol that exploits the high activity and broad substrate tolerance of lipases. This method offers a rapid and versatile route to two important PCP building blocks on gram scale, the synthetically demanding pseudo-geminal and pseudo-para PCP derivatives, obtained in good yields and with excellent enantioselectivities, and suitable for a broad range of downstream applications.[3]



Aknowledgements: We thank the Basque Government (EJ, grant IT1741-22) and Agencia Estatal de Investigación (grant PID2023-147050NB-I00//MICIU AEI/10.13039/501100011033) for financial support. D. A. acknowledges EJ for fellowship.

**Keywords:** paracyclophanes, desymmetrization, lipases, planar chirality, primary alcohols.

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# Photodriven ion transport through an Organic Mixed Ionic Electronic Conductor (OMIEC): Towards light gated ion pumps

Martin Trapero, David Mecerreyes, Ilaria Abdel Aziza, Daniele Mantione

*Student Name:* **Martin Trapero**
*PhD programme:* **Applied Chemistry and Polymeric Materials**
*Laboratory Group Name:* **Innovative Polymers Group**
*Year of enrolment:* ☐ *1st Year* ***X 2nd Year*** ☐ *3rd Year and more*

Organic Mixed Ionic-Electronic Conductors (OMIECs) enable coupled ionic and electronic transport, a property that is exploited due to its close analogy to the mechanisms underlying biological communication. [1], [2] Ion transport driven by external forces, such as applied voltage, has been extensively investigated and used for different applications, such as transistors or electrodes. [3], [4] Light-driven ion transport in OMIECs potentially offers new opportunities for wireless iontronic devices. Here we report on novel ionic conjugated polymers that convert optical stimulation into directional ionic motion. The polymers are based on a new thiophene-based monomers with multiple crosslinking points, enabling water stability, control of crosslinking density and mixed conduction. Under asymmetric visible illumination on one side, reversible photovoltages and photocurrents are generated, with polarity determined by the illumination side. These responses to light arise from coupled electronic redistribution and ion migration within the mixed-conducting matrix. As a potential application, we demonstrate a light-gated proton pump in which illumination drives directional proton flow across the film. This work establishes the use of conjugated crosslinkers, and a tunable polymer design framework for optically controlled ion transport, advancing the development of wireless iontronics.

**Keywords:** iontronics, ion transport, conjugated polymers, photo physics, ion pumps.

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# Redox Activation of Ru-Flavin Complexes

Nitin Kumar, María Jesús Móran Plata, Stefano Scoditti, Elixabete Rezabal, Luca Salassa

*Student Name:* ***Nitin Kumar***
*PhD programme: Chemistry*
*Laboratory Group Name: Inorganic Photochemistry Lab*
*Year of enrolment:* ☐ *1st Year* ☐ *2nd Year* ☒ *3rd Year and more*

In recent years, our group has demonstrated how flavins and flavoproteins can efficiently photocatalyze the activation of Pt(IV) anticancer prodrugs, including under biologically relevant conditions.[1] More recently, we have developed several redox-active metal complexes incorporating flavin and flavin-like fragments, yielding novel anticancer agents and catalysts for biologically relevant processes, such as NADH and GSH oxidation.[2-4]

Herein, we report a family of novel piano-stool Ru-riboflavin (Ru-Rf) derivatives and investigate their reactivity and photoreactivity using combined experimental and theoretical approaches (Figure 1). The Ru–Rf complexes exhibit remarkable stability in multiple solvents, as well as in DMEM cell-culture medium and human serum. In addition, they show efficient catalytic activity toward NADH oxidation. We exploited NADH-mediated reactivity to control dissociation of the monodentate Z ligand from the Ru-Rf scaffold, establishing a design principle for the chemically driven release of bioactive organic moieties within this class of systems.

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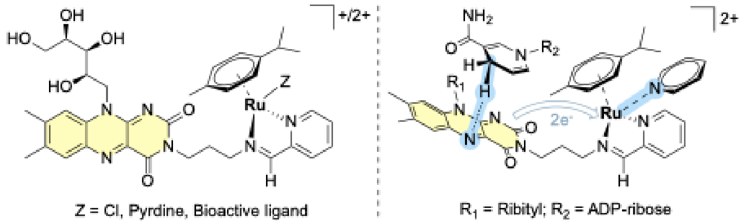

***Figure 1.*** *Schematic representation of piano-stool Ru–Rf complexes and their NADH-activation.*

**Keywords:** Ruthenium complexes, Flavin chemistry, redox activation, NADH, ligand dissociation.

**Acknowledgements:** We thank the Spanish State Research Agency (Grants PID2022-139267OB-I00 and PREP2022-000197). This work was performed under the Severo Ochoa Centres of Excellence Programme run by the Spanish State Research Agency, grant CEX2024-001494-S (DIPC).

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# Structure-Function Relationships in Electro catalytic Systems: A surface science approach

Student Name: Sruthibhai Palakkattu Kunnu Venugopalan
PhD programme: Physics of Nanostructures and Advanced Materials
Laboratory Group Name: PECAS group
Year of enrolment: □ 1st Year □ 2nd Year ✓3rd Year and more

The efficiency of sustainable hydrogen production through water electrolysis is fundamentally constrained by the slow reaction kinetics and substantial overpotentials associated with the oxygen evolution reaction (OER). Overcoming these limitations requires a molecular and atomic level understanding of how catalyst structure and electronic properties regulate adsorption energetics and reaction pathways. Establishing a structure function relationship is essential for the rational design of highly active and stable electrocatalysts for hydrogen and oxygen evolution reactions.

In this work, transition-metal single-atom catalysts (SACs) supported on nitrogen-doped highly oriented pyrolytic graphite (HOPG) are used as a model system to demonstrate how a carbon lattice provides a structurally defined and tunable coordination environment. Nitrogen doping enables precise control over the coordination of the metal center, thereby governing its electronic structure, stability, and catalytic properties. Well-defined graphitic nitrogen sites act as anchoring centers that stabilize isolated metal atoms [1] Nitrogen functionalities were incorporated into the HOPG lattice using two complementary strategies: a top-down approach based on low-energy ion implantation and a bottom-up approach employing molecular precursor assembly [2]. Both strategies produce well-defined graphitic nitrogen configurations that function as stable anchoring sites for isolated transition-metal atoms.

Subsequently, Fe, Co, and Ni were deposited under carefully controlled thermal conditions to generate atomically dispersed metal species. Low-temperature scanning tunnelling microscopy and spectroscopy (LT-STM/STS) enabled direct visualization of individual nitrogen defects and metal active sites while providing access to the local electronic structure, including shifts in the metal d-band centre. X-ray photoelectron spectroscopy further confirmed the chemical states and coordination environments of nitrogen and metal species. Distinct nitrogen configurations were found to induce characteristic electronic signatures and govern transition metal adsorption behaviour. Correlations between local electronic structure and metal support interactions reveal how modulation of the d-band centre can tune adsorption energetics of key reaction intermediates. Overall, this study establishes a reproducible, descriptor based platform for the rational design of single-atom catalysts for efficient and sustainable hydrogen production [3]

**Keywords:** Single atom catalysts, Transition metal atom, Descriptors

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# Towards the Identification of the Receptor of (+)-Conagenin

Ioritz Arburua and Antonia Mielgo

*Student Name:* Ioritz Arburua Leonis
*PhD programme:* Kimika Sintetiko eta Industriala
*Laboratory Group Name:* Katalisi Asimetrikoa
*Year of enrolment:* ☐ *1st Year* ✓*2nd Year* ☐ *3rd Year and more*

(+)-Conagenin is a low-molecular-weight immunomodulator originally isolated from the fermentation broth of *Streptomyces roseosporus*. It exhibits a broad range of biological activities, including the enhancement of the antitumor efficacy of chemotherapeutic agents such as Adriamycin and Mitomycin C.[1] Its activity has been associated with T-cell interactions, promoting lymphokine production and T-cell proliferation. However, its molecular target remains unknown, which limits its further development as a therapeutic agent.

Building on a previously reported stereoselective synthetic route developed in our group,[2] which provides efficient access to (+)-Conagenin via a key aldol reaction of α-ketoamides, this work focuses on the development of chemical tools for the identification of its molecular target. Specifically, this work pursues two main objectives: (i) the optimization of a protocol for the biotinylation of (+)-Conagenin and (ii) the identification and characterization of its putative receptor. Furthermore, the application of this synthetic methodology may enable the preparation of structural analogues of (+)-Conagenin, thereby facilitating the identification of more potent derivatives and the study of their pharmacokinetic properties and structure–activity relationships (SAR).

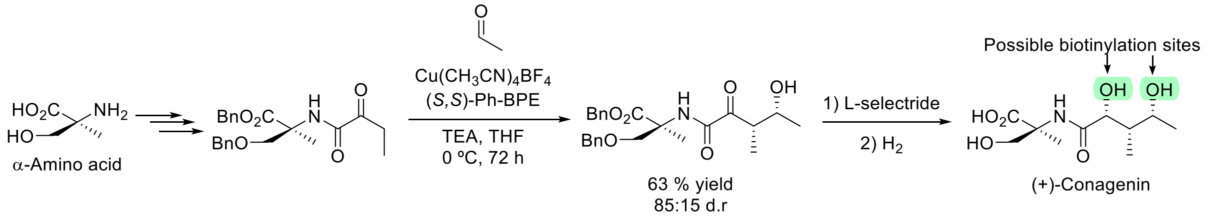

***Figure 1.*** *Shortened route of (+)-Conagenin synthesis via stereoselective aldol-reaction of α-Ketoamides and indication of plausible sites for biotinylation.*

**Keywords:** Asymmetric catalysis, Antitumoral, Cu(I), Phosphorus ligand, Enantioselective.

**Acknowledgements:** We thank Agencia Estatal de Investigación (grant PID2022-137153NB-C21/AEI/10.13039/501100011033) for financial support. I.A. thanks EHU for a predoctoral fellowship.

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# Hybrid Electrolytes Optimization by Rheology-Guided Extrusion for Solid-State Lithium Batteries

I. Varona, J. Hilhorst, T. de Heer, N. Aramburu, M. Fernández, I. Villaluenga

*Student Name:* Iker Varona
*PhD programme:* Doctorado en Química Aplicada y Materiales Poliméricos
*Laboratory Group Name:* Inorganic-polymer hybrid and nanostructured materials
*Year of enrolment:* ☐ *1st Year* ☐*x 2nd Year* ☐ *3rd Year and more*

Solid-state lithium batteries are a promising alternative to overcome the current lithium-ion technology limitations (safety concerns, flammable liquid electrolytes) in the automotive industry. Nowadays, the race in solid-state lithium batteries is centred on creating new high-performance electrolytes and electrodes at room temperature [1]. However, another concern in the battery community is the fabrication processes that are used to make these components, and their own sustainability. Extrusion processing is a relatively new sustainable alternative process that saves cost, energy, and waste disposal in battery field. In electrolyte extrusion process, the ion transport properties are governed by microstructure and viscoelastic response, which will influence in the battery performance [2]. Nevertheless, the rheological effect on the extrusion parameters selection has never been studied so far, making a try and error approach the optimization of solid electrolytes such as inorganic-polymer hybrid electrolytes. This work focuses on the development of a novel rheology-guided extrusion approach for inorganic-polymer hybrid electrolytes. $Li_3InCl_6$ (LIC) is used as inorganic part together with several non-polar homopolymers (PIB, PP and LDPE) to get solid hybrid electrolytes. The hybrid electrolytes are obtained by mixing the inorganic and the polymer in the extruder at different temperatures. Thus, we combine the high ionic conductivity and mechanical stability from the inorganic with the processability properties from the polymer. We obtained the best ionic conductivity at a defined viscosity with a LIC/LDPE hybrid, so we took it as ideal viscosity and now we are trying to replicate it with different LIC-Polymer hybrids in the extruder.

**Keywords:** hybrid, electrolyte, viscosity, conductivity, extrusion

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# Mechanistic Insights into Transfer-Dominated Branching Radical Telomerization through Kinetic Monte Carlo Simulation

Oihan Lamarins[1], Shaghayegh Hamzehlou[1]*, Nicholas Ballard*[1,2]
[1]POLYMAT, Kimika Aplikatua Saila, Kimika Fakultatea, University of the Basque Country UPV/EHU, Joxe Mari Korta Center, Avda. Tolosa 72, 20018 Donostia-San Sebastián, Spain
[2] IKERBASQUE Basque Foundation for Science, Bilbao, Spain

*Student Name: Lamarins Oihan*
*PhD programme: Applied chemistry and polymeric materials*
*Laboratory Group Name: Polymerization Processes Group      Year of enrolment:   2nd Year*

Polymethacrylates are used in many everyday products with a broad range of applications including optics, aerospace, biomedical, construction, coatings, and adhesives. However, like many plastics, they can persist in the environment for a long time after disposal. One promising approach to reduce their environmental impact is to design them so they can break down more easily at the end of their life through the introduction of labile/cleavable bonds into the polymer backbone. Among different techniques, introduction of cleavable heteroatoms can be achieved through the recently described Transfer-dominated Branching Radical Telomerisation (TBRT) strategy. TBRT enables the synthesis of step-growth like polymers by free radical polymerization of multivinylic monomers in the presence of high amounts of a chain transfer agent, resulting in the formation of branched polymers containing a polyester-like structure in the backbone[1]. However, the process is complex and therefore it remains challenging to target specific polymeric structures. To overcome this challenge, this work proposes a mechanistic study on a conventional divinyl monomer (EGDMA) – chain transfer agent (Dodecanethiol) system using the Kinetic Monte Carlo (KMC) simulation method *(Figure 1).* Utilizing detailed microstructural data, the model offers a deeper understanding of the formation of polymer network structures[2]. The predictions by KMC confirm a branched yet largely homogeneous structure, presenting cleavable ester bonds in the polymer backbone. This mechanistic study on TBRT is expected to provide clarification on the system and become a valuable tool in the development of advanced materials for future applications.

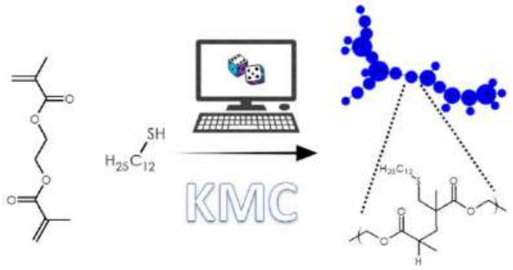

Figure 1. Representative TBRT network predicted by KMC simulation

**Keywords:** Degradability, Monte Carlo simulation, Transfer-dominated Branching Radical Telomerisation

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# Enhancing processability of PLA/PBSA blends for packaging applications

Iosu Burgaña, Shafi Alam, Ainara Sangroniz, Victor Sebastián, Gonzalo Guerrica-Echevarría, Alba Gonzalez, Lourdes Irusta, Itziar Otaegi, Nora Aranburu

*Student Name:* Iosu Burgaña
*PhD programme:* Applied Chemistry and Polymeric Materials
*Laboratory Group Name:* Polymer Technology
*Year of enrolment:* ☐ *1st Year* ☐ *2nd Year* ■ *3rd Year and more*

The environmental impact associated with the production of petroleum-based polymers has led to the growing use of biopolymers derived from renewable sources. Polylactic acid (PLA) is one of the most promising biopolymers due to its excellent biodegradability, mechanical properties, and processability [1]. However, its low ductility limits the use of PLA in film production for packaging applications [2]. Previous works in our Group [3,4] have demonstrated that blending PLA with poly(butylene succinate-co-adipate) (PBSA), an aliphatic biodegradable polymer with good ductility and processability, effectively addresses this limitation. However, one of the most promising compositions, an 80/20 PLA/PBSA blend, was difficult to process via blown film extrusion, resulting in films that could not achieve the desired thickness. This processing challenge is believed to be due to compatibility issues and the low melt strength of the blend. Previous studies have suggested that enhancing the melt strength could solve this issue, with chain extenders offering a potential solution [5]. To investigate this further, two different commercial additives were added: an acrylic melt strength enhancer (Paraloid BPMS 265) and a chain extender based on a PLA oligomer (OLA5028). Morphological analysis revealed that Paraloid promoted finer PBSA particle size and better dispersion than OLA. Moreover, Paraloid significantly enhanced ductility of the pure PLA with small reductions in stiffness and resistance. In contrast, OLA yielded a more limited ductility improvement but successfully maintained the stiffness of the pure PLA. When adding both, their effects overlapped in both morphological and mechanical properties.

**Keywords:** PLA, PBSA, blown-film extrusion, processability, structure-properties relationship

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# Interpenetrating Gel Polymer Electrolytes: Effects of PEO Structural Design

Valentina Colli, Agustín Iborra, Jorge E. Thomas, Juan M. Giussi

Student Name: Valentina Colli
PhD programme: (Visiting Student, YPF TECNOLOGÍA/Universidad Nacional de La Plata, Argentina)
Laboratory Group Name: Innovative Polymers Group
Year of enrolment: □ 1st Year □ 2nd Year X 3rd Year and more

Over the last decade, lithium-ion batteries (LIBs) have expanded into high-performance applications, owing to their high energy density, low weight, and long cycle life. However, the use of flammable organic liquid electrolytes presents significant safety concerns. In response, polymer electrolytes have emerged as safer alternatives, offering low flammability, enhanced thermal stability, and reduced leakage risk. Particularly noteworthy are gel polymer electrolytes (GPEs) which consist of a polymer matrix swollen with liquid solvents, lithium salts, and functional additives.[1] Ionic conduction primarily occurs through the liquid phase, while the polymer network provides mechanical integrity. Among the most studied polymer matrices are those based on polyethylene oxide (PEO), valued for their chain flexibility, electrochemical stability, low glass transition temperature (*Tg*), and high salt solubility. Nonetheless, their low room-temperature conductivity and limited mechanical and thermal robustness restrict their practical deployment.[2]

In this study, polymers were synthesized via Atom Transfer Radical Polymerization (ATRP), using monomers with varying ethylene oxide side chains. GPEs were formulated with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) as the salt, propylene carbonate (PC) as the plasticizer, and crosslinking agents. The materials were characterized using Differential Scanning Calorimetry (DSC), and Thermogravimetric Analysis (TGA). Ionic conductivity of the electrolytes was evaluated via Electrochemical Impedance Spectroscopy (EIS). Conductivity values on the order of $10^{-3}$ S/cm were obtained, surpassing those reported for PEO/LiTFSI systems at room temperature ($10^{-5}$ S/cm). The most promising formulation was further evaluated in lithium-metal cells, yielding a lithium transference number ($t_{Li^+}$) of 0.8. Linear Sweep Voltammetry (LSV) confirmed electrochemical stability up to 4.4 V.

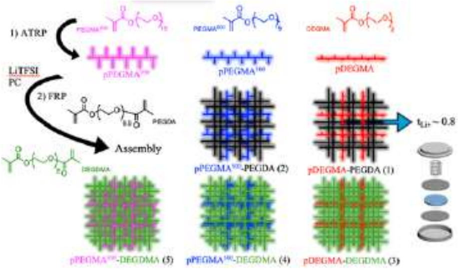

***Figure 1.*** *Schematic representation of the GPEs prepared.*

**Keywords:** Controlled Polymerization, Polymer Electrolytes, Lithium Batteries.

**References**

[1] Mecerreyes, D. *et al.*, *Macromolecular Chemistry and Physics*, 2020, 221, 1900490.

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# NEW SYNTHESIS PATHWAYS OF SUSTAINABLE POLYURETHANES WITH BARRIER PROPERTIES

Akshaya Maria Prasad, Ainara Sangroniz Agudo, Haritz Sardon

*Student Name: Akshaya Maria Prasad*
*PhD programme: Applied Chemistry and Polymers*
*Laboratory Group Name: Catalysis and sustainable polymers*
*Year of enrolment: ☐ 1st Year ☐ 2nd Year ☐ 3rd Year and more*

Waterborne polyurethane dispersions are promising environmentally friendly alternatives to solvent based coatings; however, achieving oxygen-barrier performance comparable to solvent systems remains a significant challenge. This work investigates how polymer backbone chemistry, ionic stabilization, and dispersion morphology influence the oxygen barrier properties of polyurethane dispersions intended for coating applications. The influence of diisocyanate structure and internal emulsifier concentration was evaluated to understand their effects on dispersion stability, particle size, and film properties. Polymer formation and reaction progress were verified using FTIR and NMR spectroscopy, while the physical characteristics of the dispersions were analyzed using DLS, DSC, and oxygen transmission rate (OTR) measurements. The results show that although stable dispersions can be achieved through appropriate ionic stabilization, the oxygen barrier performance of waterborne systems is limited by pathways formed during particle coalescence in film formation rather than by polymer backbone chemistry alone. To address this limitation, current work focuses on systematic formulation and processing modifications of a benchmark polyurethane dispersion system to better control dispersion morphology and improve oxygen barrier performance in waterborne polyurethane coatings.

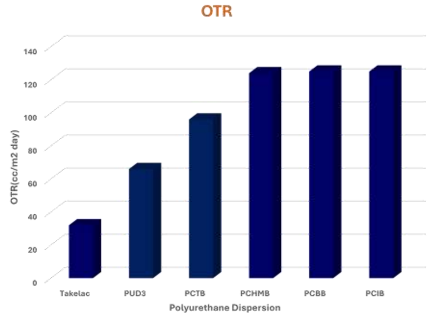

***Figure 1.*** *OTR values of different polyurethane dispersions compared with the benchmark.*

**Keywords:** Polyurethane, Waterborne polyurethane dispersion, Barrier properties, Oxygen transmission rate

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# Designing (de)bonding chemistries in coatings and adhesives for recycling of the substrates

Amirhossein Enayati, Aitor Barquero

*Student Name: Amirhossein Enayati*
*PhD programme: Applied chemistry and Polymeric Materials*
*Laboratory Group Name: POLYMAT, Polymerization Processes Group (PPG)*
*Year of enrolment:* ☐ *1st Year* ☑ *2nd Year* ☐ *3rd Year and more*

Polymeric coatings and adhesives ensure superior performance, extended lifespan, and aesthetic excellence across packaging, automotive, and construction industries. Traditional carbon-carbon backbones burden our carbon footprint through end-of-life non-recyclability. De-bonding chemistries offer a transformative solution for direct substrate recovery [1]. Lipoic acid (LpA) is a cheap, fully bio-compatible cyclic monomer from health supplements that copolymerizes with methyl methacrylate and n-butyl acrylate via industrial-scale semi-batch emulsion polymerization, delivering dynamic disulfide bonds through radical ring-opening [2]. Comprehensive fundamental studies reveal that sulfur incorporation, even at small molar ratios up to 5 mol%, precisely control selective degradation for on-demand recycling. Excellent LpA incorporation enables dramatic molar mass reduction via TCEP-mediated thiol-thiol exchange at room temperature using only water-based solution, without catalysts highly industry favorable. Controlled monomer incorporation ratios yield tunable mechanical and thermal properties for diverse adhesive and coating applications. This scalable platform transforms acrylic coatings from environmental liabilities into recyclable circular assets, directly addressing global challenges to carbon reduction by 2050.

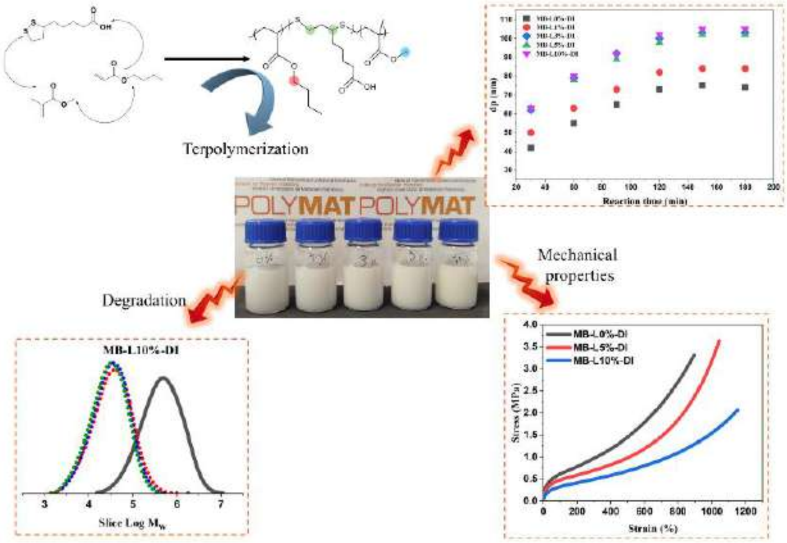

**Figure 1:** Synthesis and characterization of LpA-containing terpolymers before and after degradation.

**Keywords:** Emulsion Polymerization, Coatings, Carbon footprint, Circular economy, Sustainability

## References

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# *Late-Stage C−H Sulfonylation of Simple Phenols and Phenol-Containing Biomolecules*

Martin Villamor[1], Carlota Girón-Elola[1], Arkaitz Correa[1]

[1] *University of the Basque Country (UPV/EHU), Department of Organic Chemistry I, Joxe Mari Korta R&D Center, Avda. Tolosa 72, 20018 Donostia-San Sebastián (Spain).*

*Student Name:* Martin Villamor Garcia
*PhD programme:* Química Sintética e Industrial
*Laboratory Group Name:* Catálisis Sostenible: Métodos y computacional
*Year of enrolment:* ☒ *1st Year* ☐ *2nd Year* ☐ *3rd Year and more*

Late-stage C−H functionalization is an efficient methodology used in drug discovery and organic synthesis that enables the rapid diversification of vast libraries of analogues of existing molecules in a more effective manner.[1] Given the significance of phenols in both natural and industrially relevant compounds, the advancement of effective late-stage derivatization strategies for these scaffolds is of significant interest.[2] Our group has developed several approaches in a late-stage fashion for the bioconjugation of tyrosine (Tyr) residues,[3a-d] within structurally complex peptides. Seeking to leverage the inherent electronic reactivity of the phenolic moiety, herein we report a protocol for the direct and selective *ortho*-sulfonylation of phenol-containing biomolecules and complex peptides in the absence of directing groups (DG).

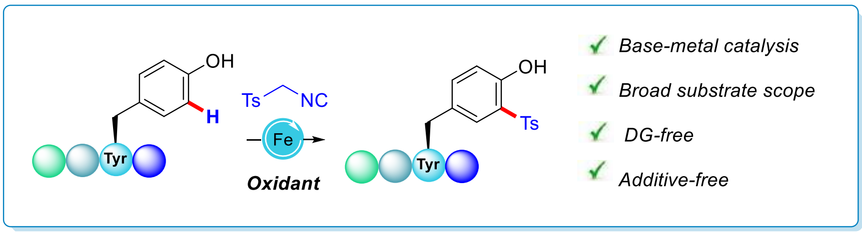

***Figure 1.*** *Late-stage C−H sulfonylation of phenol containing biomolecules.*

**Keywords:** Radical C−H functionalization, phenolic biomolecules, late-stage functionalization

## References

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# Extensional and microrheological characterization of HA solutions for 3D printing processing

Itziar Insua, Francisco J. Galindo-Rosales, Laura Campo-Deaño, Robert Aguirresarobe, Mercedes Fernández and Itxaso Calafel

*Student Name: Itziar Insua*
*PhD programme: Applied chemistry and polymeric materials*
*Laboratory Group Name: Rheology and advanced manufacturing*
*Year of enrolment: ☐ 1st Year ☐ 2nd Year X 3rd Year and more*

The development of synthetic scaffolds that accurately mimic the complex architecture of human tissue remains a primary challenge in regenerative medicine. Double-network (DN) hydrogels, which combine physical and chemical networks, aim to bridge the gap between natural tissues and laboratory-engineered constructs. In these systems, hyaluronic acid (HA) is frequently employed due to its intrinsic biocompatibility and bioactivity. [1] However, the rheological performance, functionality and additive manufacturing viability of HA are governed by its molecular weight (MW). While low-MW HA permeates tissues and promotes angiogenesis, the network entanglement for DN formation requires the higher MW provided by medium and high-MW HA, offering sustained hydration and barrier properties. [2,3]

Within this context, we characterize the shear viscoelasticity and extensional rheology of HA-based precursor resins for 3D printing applications. Through particle-tracking microrheology and capillary breakup extensional rheometry, we analysed how HA concentration and solvent (water, PBS and pre-printing resin) influence bulk viscoelasticity and apparent extensional relaxation times. The analysed data shows that the solvent medium significantly alters the extensional behaviour of HA solutions. Replacing water with a printing resin increases sensitivity to HA concentration, leading to measured apparent extensional relaxation times that rise substantially above those observed in purely aqueous environments. Microrheology measurements reflect a similar shift, showing that these systems require precise optimization as the water-based dynamics do not directly translate to the resin environment.

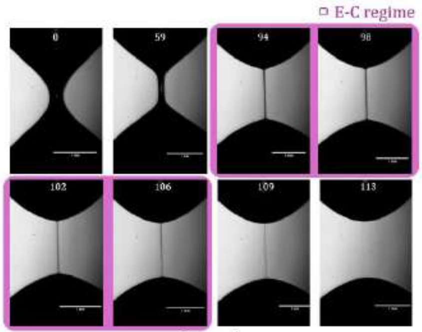

***Figure 1.*** *Filament formation and evolution until breakup for 0.6% HA solution in water.*

**Keywords:** rheology, solutions, HA, hydrogels, 3D printing

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# Molecular Pathways of LCST and UCST Behavior in Ionic Liquid water mixture

Hussen O. Mohammed, Abel de Cozar, Ronen Zangi

*Student Name: Hussen Oumer*
*PhD programme: Synthetic and industrial Chemistry*
*Laboratory Group Name: Computational Biophysical chemistry*
*Year of enrollment: ☐ 1st Year [✓ ☐ 2nd Year] ☐ 3rd Year and more*

We investigate liquid–liquid phase separation (LLPS) of thermoresponsive ionic liquid (IL)-water mixtures through atomistic molecular dynamics simulations. Two model systems are studied: tetrabutylphosphonium 2,4,6 -trimethylbenzenesulfonate, $[P_{4444}][TMBS]$[1], which exhibits a lower critical solution temperature (LCST) phase separation, and protonated betaine bis(trifluoromethylsulfonyl)imide, $[Hbet][Tf_2N]$, which displays an upper critical solution temperature (UCST) behavior [2]. In both cases, down scaling of the unit ionic charges by a factor of 0.95 was necessary to reproduce the temperature-composition phase diagrams qualitatively. With this model, the spontaneous emergence of the IL-rich and water-rich phases of the biphasic states obtained in the simulations are characterized by compositions that are in excellent agreement with experimental findings. Dynamical properties of these systems, such as viscosities, were slightly retarded (larger by a factor of 2-5) in comparison with experimental values. Aiming to elucidate the driving forces governing the two types of phase separation diagrams, we performed detailed analysis of energy decompositions, hydrogen-bonding networks, and microstructural organizations. We find that for $[P_{4444}][TMBS]$/water phase demixing, increasing temperature weakens IL–water hydrogen bonds, augments the enthalpic penalty of hydration, and favors ion pairing and mesoscale segregation. Conversely, for $[Hbet][Tf_2N]$/water demixing, cooling enhances water self-networking and suppresses ion hydration, promoting like-like association and a polar domain growth, while heating disrupts the water network and re-establishes miscibility through stronger ion-water hydrogen bonding (anion > cation). By elucidating these molecular-level mechanisms underlying LCST and UCST behavior in distinct ILs, this study offers a predictive, simulation-based framework for the rational design of thermoresponsive draw solutes in forward osmosis desalination, enabling tunable and energy-efficient regeneration cycles.

**Keywords:** Ionic Liquids, MD simulation, Lower Critical Solution Temperature (LCST), Upper Critical Solution Temperature.

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# Deconstructing α-Aminoalkyl Sulfones as Dual *d*-Sulfonyl/*α*-Azomethine Synthons: Synthesis of 3-Sulfonylmethylindole Aminals

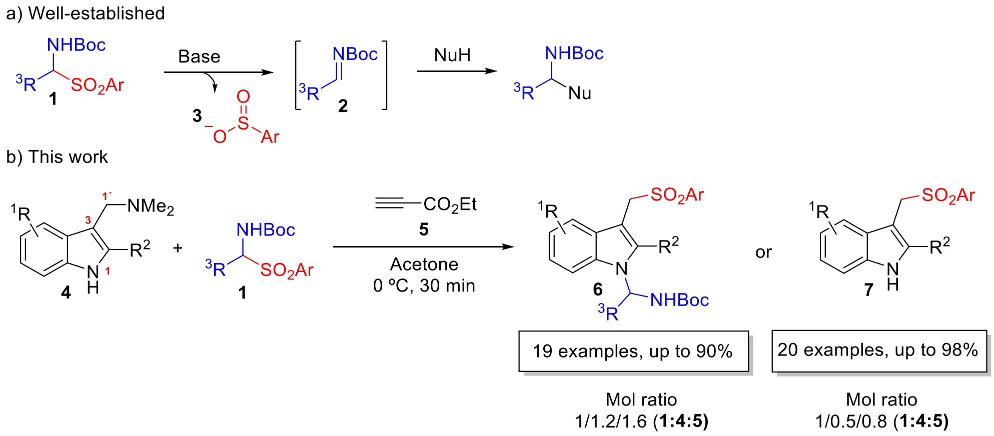
A. Mujika,[a] G. Dominguez,[a] I. Hernández,[a] V. A. Soloshonok,[a] A. Landa,[a] and M. Oiarbide[a]

[a] *Department of Organic Chemistry I, Universidad del País Vasco UPV/EHU*

*e-mail: anje.mugica@ehu.eus*

*Student Name: Anje Mujika Aztiria*
*PhD programme: Synthetic and Industrial Chemistry*
*Laboratory Group Name: Asymmetric catalysis*
*Year of enrolment: 1st Year*

α-Amido sulfones **1** have been widely applied as a synthetic equivalent of the electrophilic azomethine synthon **2**. Bases can promote the release of the *N*-acyl imine **2** for subsequent *in situ* coupling with a variety of nucleophiles. In all these procedures, the concomitantly generated aryl(alkyl)sulfinyl fragment **3** does not get incorporated into the target molecule thus becoming waste material. In this study we demonstrate that this mainstream reactivity of α-amido sulfones may be upgraded making feasible for the first time the full incorporation of both the amidoalkyl and organosulfonyl functionalities of **1** onto the reaction target. To showcase this dual reactivity of **1**, we selected gramines **4** as complementary acceptor/donor reaction partner. It was gratifying to observe that, in the presence of ethyl propiolate **5** as the activator, gramines smoothly react with α-amido sulfones **1** to furnish 3-sulfonylmethylindole aminals **6** in high yields. A critical aspect of our findings is the exceptional control achieved over reaction selectivity by adjustment of the reactants' molar ratio. Thus products **7** could be obtained as alternate products by using a 1/0.5/0.8 molar ratio of **1:4:5**. Factors that control this reaction divergence as well as a whole mechanistic proposal, including the plausible role played by excess gramine during formation of aminal **6** will be presented.



**Keywords:** *α-Amido sulfones*, *gramines, deaminative coupling, aminals. dual reactivity*

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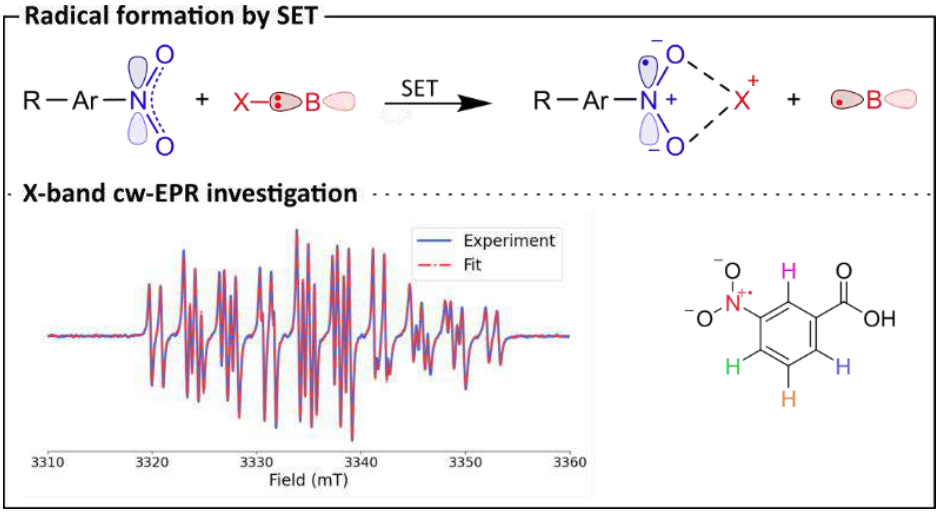
# SET – driven radical formation in nitroaromatics

L. Ebo, S. Balahoju, J. Marvizón Valera, I. Zubillaga Nogueira, N. Bhattacharjee, L. Lezama, D. Reta

*Student Name: Lisa Ebo*
*PhD programme: Materials Science and Technology*
*Laboratory Group Name: Polymers and advanced materials*
*Year of enrolment:* ***x 1st Year*** ~~☐ *2nd Year*~~ ~~☐ *3rd Year and more*~~

Knowledge of radical electronic structures enables the control of their properties and opens the potential of fine controlling their reactivity. Therefore, EPR is an unmatched technique, needed for the electronic structure characterization of organic radicals. However, the reactive nature of radicals and non-trivial preparational requirements limit the number of usable radical species until now. Enabling the generation of radical species under simple reaction conditions, employing available and inexpensive reactants, is therefore the key component for harnessing the extraordinary properties of organic radicals. In our recent work on nitrobenzene, we uncovered a radical formation process by a thermal single electron transfer (SET) from multiple anionic organo-bases1. I will show how the scope of this SET-driven radical formation can be expanded to the wider family of nitroaromatics, employing cw-EPR spectroscopy and DFT calculations. The under-standing of the electronic structures of these radical pairs enables the utilization of radical compounds as reacting agents under mild synthetic conditions, laying the foundation for a new class of distinctive reaction mechanisms and thus unexplored opportunities in organic synthesis.



**Keywords:** single electron transfer (SET), organic radicals, Nitroaromatics

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# Voltage-Dependent Hydrogen Evolution on PtGe Surfaces

Idoia Camara, Elisa Jimenez-Izal and J.M. Mercero

*Student Name:* Idoia Camara Garmendia
*PhD programme:* Programa de Doctorado en Química Teórica y Modelización Computacional.
*Laboratory Group Name: Polimero eta Material Aurreratuak: Fisika, Kimika eta Teknologia Saila*
*Kimika Fakultatea, Universidad del País Vasco (UPV/EHU)*
*Year of enrolment:*

■ *1st Year* ☐ *2nd Year* ☐ *3rd Year and more*

The hydrogen evolution reaction (HER) is a key process for sustainable hydrogen production and plays a central role in the energy transition [1]. Although platinum remains the benchmark catalyst, reducing noble metal content while preserving high catalytic activity is essential for scalable applications. In this work, we investigate the catalytic performance of the platinum-germanium surface (PtGe)[2] as a potential HER electrocatalyst under realistic electrochemical conditions. Density Functional Theory (DFT) calculations were carried out within a grand canonical ensemble framework to explicitly control the electrode potential, in combination with an implicit electrolyte model including explicit solvent configurations through the Eigen cation ($H_9O_4^+$). Activation energies for the elementary Volmer, Heyrovsky and Tafel steps were determined via the Nudged Elastic Band method under applied electrochemical potentials. Hydrogen adsorption occurs preferentially on Pt sites with near-thermoneutral adsorption energies, while Ge atoms contribute to surface stabilization. The Volmer barrier shows a strong voltage dependence, decreasing from 0.65 eV at 0 V to 0.08 eV at -1.0 V, whereas the Heyrovsky step remains rate-limiting across the studied potentials. At high hydrogen coverage, the Tafel pathway becomes competitive, indicating a mechanism shift depending on potential and surface coverage. These findings highlight the importance of explicitly accounting for electrochemical conditions in computational catalysis and suggest that PtGe surfaces constitute a promising platform for HER optimization.

**Keywords:** Hydrogen Evolution Reaction (HER), PtGe surface, Density Functional Theory (DFT), Electrochemical potential, HER mechanism.

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# DNA-based Catalysis Membrane Reactor

Hélia Ventribout Rodríguez

*Student Name: Hélia Ventribout Rodríguez*
*PhD program: Applied Chemistry and Polymeric Materials*
*Laboratory Group Name: NanoBioSeparations (Prof. Thomas Schäfer)*
*Year of enrollment: X 1st Year ☐ 2nd Year ☐ 3rd Year and more*

DNA-based catalysts offer remarkable enantioselectivity thanks to DNA double helical chiral structure, but are typically limited to small-scale batch reactions in industrial processes. First results demonstrates successful translation of a benchmark Diels-Alder reaction to continuous-flow conditions using soluble Cu(II)-ligand-modified DNA in a water/DMSO co-solvent system, achieving 75% yield and 96% enantiomeric excess (6h, 22°C), comparable to batch performance and confirming catalyst integrity under flow. Next step include DNA-catalyst immobilization, for this, quartz crystal microbalance with dissipation (QCM-D) and surface plasmon resonance (SPR) quantify real-time binding kinetics, affinity and stability of DNA-catalyst assemblies on nanoporous inorganic/polymeric membrane surfaces. Circular dichroism (CD) spectroscopy verifies preservation of the DNA double helix and chiral microenvironment across solvent compositions, while chiral high-performance liquid chromatography (HPLC) delivers precise reaction analytics. Current efforts focus on immobilizing high DNA-catalyst loadings within membranes pores and engineering an integrated reactor module for continuous/semi-continuous flow operations. This proof-of-concept will validate enhanced mass transfer, and allow catalyst reuse. Ultimately, the modular design targets adaptation for diverse industrially relevant asymmetric transformations, establishing DNA-based catalysis within a scalable, sustainable membrane reactor platform.

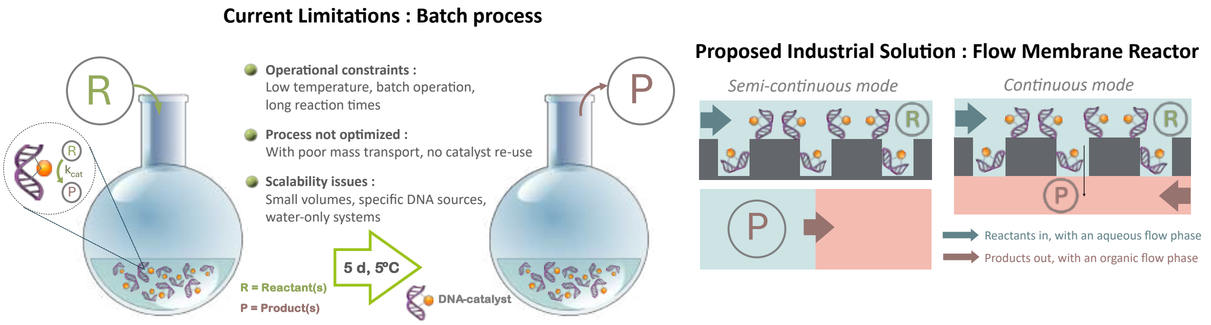

***Figure 1.*** *From batch process limitations to continuous membrane flow reactor for DNA-based asymmetric catalysis.*

**Keywords:** DNA-based catalysis, membrane modification, reactor engineering, enantioselectivity

## References

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# Co-Catalyzed Intramolecular C–H Alkylamination of Tyrosine Derivatives

Nerea Cirauqui[1], Iván Pérez-Cubero [1], Arkaitz Correa[1]

[1]*University of the Basque Country (UPV/EHU), Department of Organic Chemistry I, Joxe Mari Korta R&D Center, Avda. Tolosa 72, 20018 Donostia-San Sebastián (Spain)*

*Student Name: Nerea Cirauqui Guillén*
*PhD programme: Química Sintética e Industrial*
*Laboratory Group Name: Catálisis Sostenible: Métodos y Computacional.*
*Year of enrolment:* ■ *1st Year* □ *2nd Year* □ *3rd Year and more*

In the past decade, the use of late-stage functionalization has been exponentially increasing, especially in peptide chemistry.[1] In our group several methods for the metal-catalyzed C($sp^2$)–H functionalization have been developed,[2] however, its application to the synthesis of molecules of high structural complexity remains a challenging task of prime synthetic relevance. Based on the previously developed protocol for the radical amination of phenol-containing biomolecules[3] and our recent experience in the assembly of cyclopeptides,[4] a cobalt-catalyzed radical macrocyclization for a variety of Tyr-containing compounds bearing piperazines is currently being optimized. This approach uses $Co(acac)_2{\cdot}H_2O$ as the catalyst, thereby enabling the C–N coupling at the *ortho* C–H bond of phenols in a late-stage fashion. This operationally simple coupling technique can proceed intramolecularly to deliver unconventional cyclopeptides.

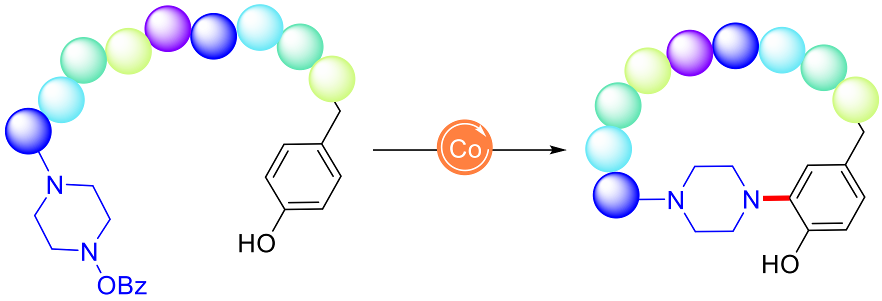

***Figure 1.*** *Reaction conditions for the formation of cyclopeptides.*

**Keywords:** Cyclopeptides, Tyrosine, C–H Functionalization, Catalysis.

**Acknowledgment:** We are grateful to Ministerio de Ciencia e Innovación (PID2021-122889NB-I00 and PID2024-158303NB-I00, by MCIN/AEI/10.13039/501100011033) and Basque Government (IT1741-22) for financial support. We thank for technical and human support provided by SGIker of UPV/EHU and European funding (ERDF and ESF).

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# ADVANCED SURFACE MODIFICATION FOR AUTOMOTIVE POLYMER ADHESION

Asier de Santos Larrañaga, Guillem Seychal, Iñigo Calvo, Haritz Sardon

*Student Name: Asier de Santos Larrañaga*
*PhD programme: Química Aplicada y Materiales Poliméricos*
*Laboratory Group Name: Catalysis and Sustainable Polymers*
*Year of enrolment: x 1st Year ☐ 2nd Year ☐ 3rd Year and more*

*The automotive industry increasingly demands lightweight materials with superior bonding performance for multi-material assemblies. Polybutylene terephthalate (PBT) is widely used in automotive applications due to its excellent mechanical properties and chemical resistance. However, its low surface energy limits adhesion performance with adhesives and coatings. Current strategies include physical activation methods and mechanical roughening, which often suffer from limited chemical selectivity and hydrophobic recovery. Wet chemical methods enable the introduction of covalently bonded functional groups with improved specificity and long-term stability. This work aims to develop chemical modification strategies to improve the adhesion properties of PBT through controlled surface functionalization via transesterification. Surface characterization was performed using ATR-FTIR and contact angle measurements. Morphological modifications were evaluated by SEM-EDX. Adhesion performance was quantified through single lap-shear tests following ASTM D1002 using 0epoxide adhesives. Surface free energy was calculated using the OWRK method, and a design of experiments was performed.*

*Chemical modification successfully introduced hydroxyl and amino groups onto the PBT surface, confirmed by ATR-FTIR analysis (1550 $cm^{-1}$ band increase). Preliminary lap-shear tests revealed complex functionalization-adhesion relationships requiring further investigation. The methodology is transferable to other automotive polymers. Future work will extend this approach to a broader range of polymers, adhesives, and adhesive promoters.*

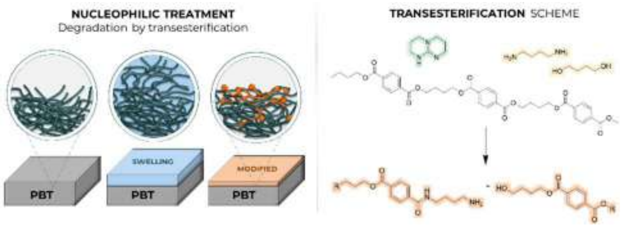

***Figure 1**. Schematic procedure of PBT functionalization*

**Keywords:** Surface modification, polybutylene terephthalate (PBT), adhesion bonding of polymers, lap-shear, Transesterification.

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# Assessment of filamentous fungi with dye-degrading potential isolated from Basque estuaries

Ziortza Agirrezabala[1], Ainara Otamendi[1], Laura Alonso-Sáez[2], Miren Ostra[3], Oier Etxebeste[1]

[1]Laboratory of Biology, Department of Applied Chemistry, Faculty of Chemistry, University of the Basque Country (UPV/EHU), 20018 San Sebastian; ziortza.agirrezabala@ehu.eus
[2]AZTI, Marine Research, Basque Research and Technology Alliance (BRTA), Sukarrieta
[3]Laboratory of Analytical Chemistry, Department of Applied Chemistry, Faculty of Chemistry, University of the Basque Country (UPV/EHU), 20018 San Sebastian

*Student Name: Ziortza Agirrezabala Urkia*
*PhD programme: Applied Chemistry and Polymers*
*Laboratory Group Name: Microbiology. Applied Chemistry*
*Year of enrolment: □ 1st Year □ 2nd Year X 3rd Year and more*

Contamination of aquatic environments has become a big issue over the last years[1,2]. Coloured wastewater effluents released by several industries, especially the textile sector, may not only be mutagenic, carcinogenic, or toxic, but also block light penetration into the water, restricting photosynthetic processes, inhibiting the growth of aquatic biota, and interfering with gas solubility in water[3,4]. Filamentous fungi derived from marine environments are well known as a potential genetic resource for various biotechnological applications, including bioremediation[4,5]. In this context, this work focused on the isolation of filamentous fungi from sediment samples collected from estuaries of the Basque Country. Their phenotypic characterization led to the identification of strains potentially capable of degrading industrial dyes. Three isolates belonging, based on ITS sequencing, to the genera *Acremonium* (M38), *Monodictys* (M63), and *Cladosporium* (M104) were selected for further study due to their potential to degrade and/or adsorb industrial dyes such as Remazol Brilliant Blue R (Reactive Blue 19), Congo Red (Direct Red 28), and Indigo Carmine (Acid Blue 74). Genomics, transcriptomics and proteomics analyses of those strains will provide key information on the genome features of those species and the mechanisms and activities induced for the degradation/adsorption of these dyes. In summary, this study shows that marine fungi from the Basque coast could be a valuable source for the development of new biotechnological tools for reducing dye pollution and protecting aquatic environments.

**Keywords:** Estuarine fungi, industrial dye, dye-degrading, *omics* analysis, bioremediation.

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# Sustainable and Chemically Recyclable PPeF Nanocomposites for Advanced Packaging Applications.

**Md Shafi Alam,**[a] Erlantz Lizundia[b,c], Ainara Sangroniz[a] .

*Student Name: Md Shafi Alam*
*PhD programme: Chemistry and Polymers*
*Laboratory Group Name: Ainara Sangroniz*
*Year of enrolment:* □ *3rd Year and more*

## Abstract:

Poly(pentamethylene furanoate) (PPeF) is a bio-based polyester that could be useful for making eco-friendly packaging. However its amorphous structure and weak mechanical properties limits its application in the market. In this study, PPeF was synthesized via the melt polycondensation of 2,5-furandicarboxylic acid (FDCA) and 1,5-pentanediol (PDO). Then, nanocomposites were prepared containing 5 wt% cellulose nanocrystals (CNC), cellulose nanofibers (CNF), and TEMPO-oxidized CNF (CNF-Tempo-S). DSC shows that adding nanocellulose changed the material from amorphous to semicrystalline, which means that the filler act as a nucleating agent. The mechanical properties were improved considerably. For example, Young's modulus was improved from 4.7 MPa for neat PPeF to 280 MPa (5% CNF-Tempo-S). The oxygen barrier performance of all nanocomposites were improved, but the water vapor transmission and surface wettability were very much affected by the shape and chemistry of the nanocellulose. Chemical recyclability of PPeF and its nanocomposites was analyzed through controlled chemical depolymerization, producing dimethyl furan-2,5-dicarboxylate (DMFDCA) and 1,5-pentanediol, in addition to property enhancement. Re-polymerized PPeF was similar to the neat polymer. Recycled PPeF-based nanocomposites showed even better mechanical and barrier performance, which shows that the closed-loop recycling method is strong and that can be used in advanced bio-based packaging applications.[1,2]

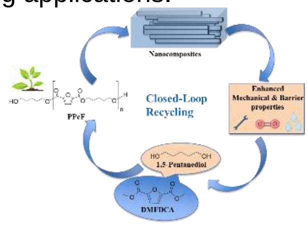

Figure 1: Graphical representation of nanocomposites development and chemical recycling.

**Keywords:** Furandicarboxylic acid; Nonocomposites; Chitin nanofiber; Food packaging; Barrier properties;.

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# Solid lipid nanoparticles: innovative tools against resistant bacteria.

Oihane Altube Urquia*[1], Maria Alonso Ferreras[1], Miren Itziar Alkorta Calvo[2], Lide Arana Urbieta[1]

*Student Name: Oihane Altube Urquia*
*PhD programme: Applied Chemistry and Polymeric materials*
*Laboratory Group Name: Biochemistry II*
*Year of enrolment: ☐ 1st Year ☐ 2nd Year ☐ 3rd Year and more*

**Rationale**: Antimicrobial resistance (AMR) represents an urgent global health challenge, requiring innovative strategies to enhance the efficacy of existing antibiotics, as many conventional antibiotics are becoming ineffective against resistant pathogens. In this work, a nanotechnology-based approach was evaluated to enhance the efficacy of rifampicin by encapsulating the antibiotic within cationic solid lipid nanoparticles (SLNs). Additionally, since bacterial conjugation is one of the main mechanisms responsible for the dissemination of resistance genes, linoleic acid—described as an inhibitor of this process—was co-encapsulated with rifampicin to develop a combined therapy integrating conjugation inhibition and antibacterial activity[1,2].

**Methods**: SLNs with varying rifampicin (0–15 mg), with or without 5 mg linoleic acid, were synthesized and characterized for size, polydispersity, zeta potential, stability, encapsulation efficiency, and drug release. IC50 assays compared rifampicin-loaded SLNs with free rifampicin in multiple bacterial strains.

**Results**: The results indicate that cationic SLNs act as effective drug carriers by improving the efficiency of the drug, facilitating its delivery and enabling a more controlled release profile. The incorporation of linoleic acid additionally provides a potentially useful component to limit the spread of antimicrobial resistance through conjugation inhibition.

**Conclusions**: In conclusion, SLNs proved to be valuable drug delivery systems, improving the efficacy and release profile of the drug. Additionally, the combined therapy with linoleic acid represents a promising strategy to address the growing challenge of antimicrobial resistance by integrating antibacterial activity with conjugation inhibition.

**Keywords:** AMR, Conjugation, SLN, Rifampicin, Linoleic acid

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# Development of waterborne paints as Passive Daytime Radiative Cooling (PDRC) materials

Janire Aramberri, Guido Goracci and Aitor Barquero

*Student Name: Janire Aramberri*
*PhD programme: Applied Chemistry and Polymeric Materials*
*Laboratory Group Name: Grupo Ingeniería Química (GIQ)*
*Year of enrolment:* ☐ ***1st Year*** ☐ *2nd Year* ☐ *3rd Year and more*

Urban population growth is intensifying the Urban Heat Island (UHI) effect, raising city temperatures and therefore, increasing energy demand with Heating, Ventilation, and Air Conditioning (HVAC) systems, which also contribute to greenhouse gas emissions [1]. Passive Daytime Radiative Cooling (PDRC) technology offers a sustainable alternative by emitting heat as infrared radiation to outer space without energy input. Current PDRC materials often rely on multilayer polymer coatings with white pigments like titanium dioxide ($TiO_2$), which can be costly and environmentally challenging due to Volatile Organic Compounds (VOC) emissions [2]. Waterborne paints present a greener alternative, reducing VOCs and enhancing the use of sustainable pigments such as cementitious materials. Among them, portlandite ($Ca(OH)_2$) shows high solar reflectivity ($R_{solar}$) and emissivity in the atmospheric window ($e_{AW}$), making it suitable for scalable and eco-friendly cooling coatings [3]. Moreover, its implementation can also promote circular economy, as it comprises a major part of alkaline paper mill waste. This project aims to deepen our understanding of radiative cooling and waterborne paint technologies by first, studying the effect on the paint performance of several parameters, to then search for the most suitable paint's components for application. We have already observed that either the Pigment Volume Concentration (PVC) and binder's stabilization system have a significant effect, improving the optical properties but compromising the film integrity if ion or pigment concentration is too high. Additionally, we are now focused on synthesizing nano-sized pigment and the most transparent binder possible to emphasize the optical properties and consequently, the cooling capacity.

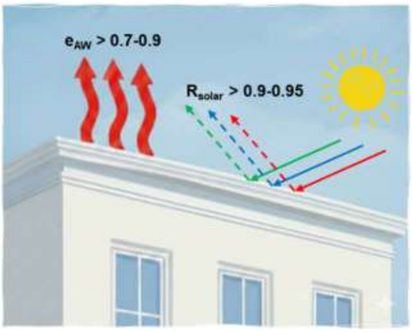

***Figure 1.*** *Mode of working of a PDRC material.*

**Keywords:** Urban Heat Island, Passive Daytime Radiative Cooling, waterborne paint, portlandite

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# Mechanistic Studies of Copper (I)-Catalyzed Enantioselective Cross Aldol Reactions of α-Ketoamides

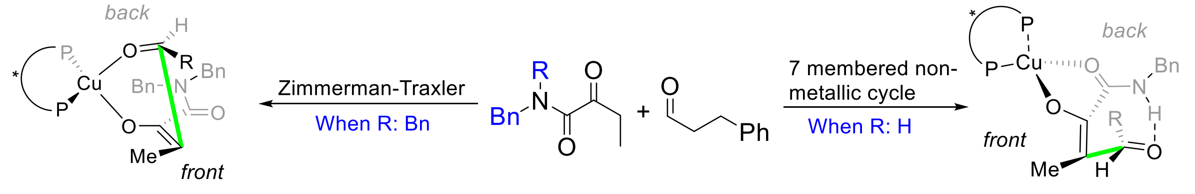
Ricardo Rodríguez, Jon Artieda, Abel de Cózar, Maria Campo and Antonia Mielgo*

Student Name: Jon Artieda Rota
PhD programme: Doctorado en Química Sintética e Industrial
Laboratory Group Name: Grupo de Investigación Catálisis Asimétrica y Síntesis Química
Year of enrolment: ☐ 1st Year ✓2nd Year ☐ 3rd Year and more

Pyruvate aldol reactions constitute a very useful tool to access γ-hydroxy-α-keto acids, which are also relevant intermediates in the biosynthesis of sialic and ulosonic acids, which play central roles in cell-cell recognition, inmune modulation and host-patogen interactions. In nature, this reaction is catalyzed by Class I and Class II enzyme aldolases, which have been mimetized by developing several enzymatic and chemical protocols. Nevertheless, this transformation is still limited to a narrow range of donors and carbonyl acceptors, being enolizable aldehydes specially challenging substrates.

We have recently found a solution to the above concerns by developing a highly stereoselective asymmetric direct cross aldol reaction of α-ketoamides triggered by a combination of Cu(I) salt, a tertiary amine base and the Pilkington´s chiral bisphosphine ligand with a broad substrate scope.

Herein, we present a comprehensive mechanistic study of this aldol reaction through kinetic and DFT studies. *N*,*N*-Disubstituted substrates react via a classical Zimmerman-Traxler transition state, whereas *N*-monosubstituted analogs proceed through an unusual outer-sphere transition state involving a 10-electron rearrangement and formation of an iminolate intermediate. Insights on reaction reversibility are also presented.



***Scheme 1.*** *Mechanisms for the cross-aldol reaction of α-ketoamides depending on the substitution of the amide moiety and insights on reaction reversibility.*

**Keywords:** retroaldol reaction, kinetic studies, DFT studies.

**Acknowledgements:** We thank Agencia Estatal de Investigación (grant PID2022-137153NB-C21/AEI/10.13039/501100011033) and Basque Government (IT-1583-22) for financial support. R.R. thanks MIU for a FPU fellowship, M.C. thanks EJ-GV and J.A. thanks EHU for a predoctoral fellowship.

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# Enhanced lithium-ion conductivity in glassy chloride solid electrolytes

C. Azabal, O. Pajuelo, I. Villaluenga

*Student Name: Claudia Azabal Martin*
*PhD programme: Applied Chemistry and Polymeric Materials*
*Laboratory Group Name: Inorganic-polymer hybrid and nanostructured materials*
*Year of enrolment: ☐ 1st Year ☐ 2nd Year ☐ 3rd Year and more*

Solid-state batteries (SSBs) are considered an ideal next-generation electrochemical energy storage system due to their potentially higher intrinsic safety and energy densities.[1] In recent years, halide-based solid electrolytes have emerged as promising materials exhibiting high ionic conductivities at room temperature and excellent operating stability up to 4.3 V.[2,3] In this work, the zirconium-based halide solid electrolytes $x\mathrm{Li_3PO_4}$-$\mathrm{ZrCl_4}$ and $x\mathrm{Li_2CO_3}$-$\mathrm{ZrCl_4}$ are synthesized via high-energy ball milling; different molar fractions (x) of each lithium salt are synthesized in order to study the structure-property relationships governing ionic conductivity in this type of materials. Electrochemical Impedance spectroscopy (EIS) and X-ray diffraction (XRD) measurements indicate that the incorporation of $\mathrm{PO_4^{3-}}$ and $\mathrm{CO_3^{2-}}$ induces a transition of $\mathrm{Li_2ZrCl_6}$ into an amorphous phase that increases the ionic conductivity of the pristine material, reaching a maximum ionic conductivity value at room temperature of 1.08 mS cm$^{-1}$ for $0.5\mathrm{Li_3PO_4}$-$\mathrm{ZrCl_4}$ and 0.62 mS cm$^{-1}$ for $0.33\mathrm{Li_2CO_3}$-$\mathrm{ZrCl_4}$. Stability tests under dry room conditions confirm that the materials retain their ionic conductivity in a water-free environment. These findings support their potential for scalable implementation in solid-state batteries at the industrial scale.

**Keywords:** All-solid-state lithium battery, inorganic solid electrolyte, ionic conductivity.

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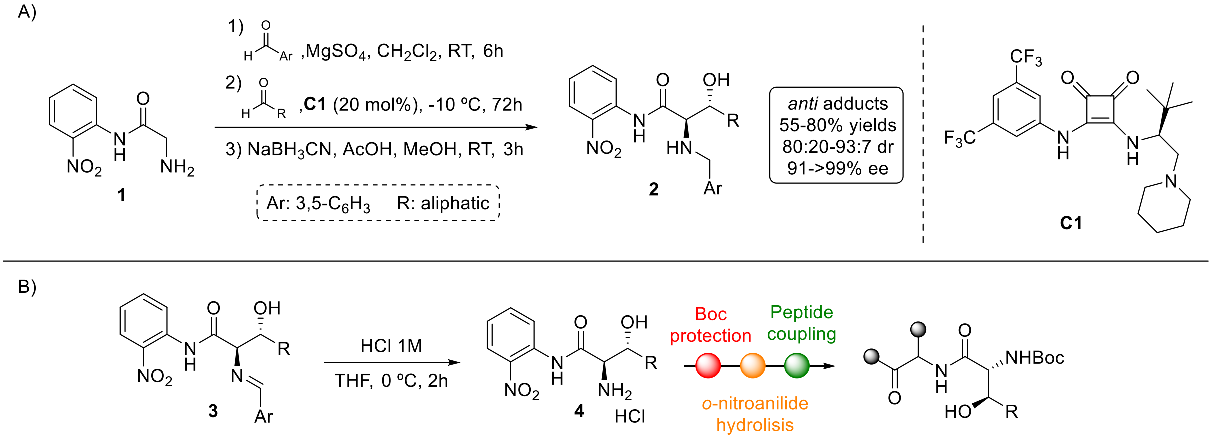
# *anti*-Selective Cross-Aldol Reactions of Schiff Bases of Glycine *o*-Nitroanilide and Applications in Peptide Synthesis

Maria Campo, Ricardo Rodriguez-Urretavizcaya and Antonia Mielgo*

*Student Name: Maria Campo*
*PhD programme: Synthetic and Industrial Chemistry*
*Laboratory Group Name: Organic Chemistry I*
*Year of enrolment:* ☐ *1st Year* ☐ *2nd Year* ■ *3rd Year and more*

β-Hydroxy α-amino acids are compounds of interest in medicinal chemistry and useful starting materials for synthesis.[1] The most direct route for their synthesis is the aldol reaction of glycine derivatives. Our group developed the first aldol reaction of glycine Schiff bases using Brønsted base (BB) catalysis, providing *syn*-adducts with high diastereo- and enantioselectivity.[2] The key to this development was the use of a glycine *o*-nitroanilide derivative in combination with an ureidopeptide-based BB catalyst.

Herein, we report a sequential protocol for the *anti*-selective aldol reaction of glycine *o*-nitroanilide derivatives with enolizable aldehydes catalyzed by squaramide-based BB catalyst **C1**, with the corresponding aldol adducts **2** being obtained with good to excellent diastereo- and enantioselectivity (Scheme 1, A). To provide further proof of the relevance of the *o*-nitroanilide moiety as both a directing group and a convenient protecting group, different protocols were developed for amide cleavage, followed by additional peptide bond formation to incorporate the β-hydroxy α-amino acid moiety into peptide sequences (Scheme 1, B).



*Scheme 1. A) Cross-aldol reaction. B) Incorporation of the aldol derivatives into peptides.*

**Keywords:** β-Hydroxy α-amino acids, bifunctional Brønsted bases, aldol reaction, Schiff bases.

**Acknowledgments:** We thank Agencia Estatal de Investigación (PID2022-137153NB-C21/10.13039/501100011033) and Basque Government for financial support. R. R. thanks MIU for a FPU fellowship and M. C. thanks EJ-GV for a predoctoral fellowship.

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# ENGINEERED PROTEINS-NANOCLUSTER HYBRID NANOTOOLS FOR COMBINATION THERAPIES AGAINST CANCER

Eva Carpintero Cueto[1], Gabriela Guedes Faria[1], Aitziber L. Cortajarena[1,21]

Center for Cooperative Research in Biomaterials (CIC biomaGUNE), Basque Research and Technology Alliance (BRTA), Paseo de Miramón 194, 20014, Donostia-San Sebastián, Spain.; 2 IKERBASQUE, Basque Foundation for Science, Bilbao, 48009 Spain.

*Student Name: Eva Carpintero Cueto*
*PhD programme: Doctoral Programme in Applied Chemistry and Polymeric Materials*
*Laboratory Group Name:*
*Year of enrolment: □ 1st Year □ 2nd Year x 3rd Year and more*

The use of combination therapies against cancer diseases is becoming a promising approach in the clinic, as they address key challenges such as the acquisition of drug resistance. Engineered proteins offer innovative platforms for encoding these multimodal therapies. In particular, proteins based on the consensus tetratricopeptide repeat (CTPR) protein shows great potential, as their modular nature enables size tuning, while their robustness and mutation permissibility allows the addition of functional modifications in the sequence [1]. Protein binding domains that recognize target proteins in tumors can be added to the CTPR [2]. Additionally, metal nanoclusters (NCs) with functionalities such as catalytic activities or photothermal properties can be synthetized directly in CTPR modules displaying metal binding residues at strategic positions. Photothermal activity enables their use in photothermal therapy (PTT), leading to the thermal ablation of cancer cells. Simultaneously, catalytic activities, particularly catalase-like activity can take advantage of the $H_2O_2$, abundant in the tumor microenvironment (TME), to generate $O_2$, alleviating tumor hypoxia, which is closely associated with poor prognosis. Here, we present the design of a series of CTPR-nanomaterial hybrids based on CTPRs with metal-coordination modules to stabilize Au/Pt NCs with photothermal properties and specific catalytic activities. We demonstrate their ability to catalyze the disproportionation of $H_2O_2$ into $H_2O$ and $O_2$, and to induce cell death in tumor cell lines when irradiated, proving their potential for therapeutic applications.

**Keywords:** combination cancer therapy, CTPR proteins, metal nanoclusters, photothermal therapy, catalytic activity.

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# Adhesion of Conducting Polymer Electrodes for Implantable Devices

**Andrea Cid-Alonso,** Antonio Dominguez-Alfaro*, Ilaria Abdel Aziz, Sharon Monaci, Daniele Mantione, George Malliaras, David Mecerreyes*

*Student Name: Andrea Cid*
*PhD programme: Applied Chemistry and Polymers*
*Laboratory Group Name: Innovative Polymers Group*
*Year of enrolment: **X** 1st Year ☐ 2nd Year ☐ 3rd Year and more*

This research presents a dual-layer strategy to improve the stability and adhesion of conducting polymer electrodes for implantable bioelectronics. Traditionally, gold electrodes coated with PEDOT:PSS absorb water, causing increased impedance and delamination [1]. To address this, an electropolymerized thiolated PEDOT interlayer was introduced between the gold substrate and a top layer of spin-coated PEDOT:PSS [2, 3].

During the optimization of electropolymerization parameters, $LiClO_4$ proved to be more effective as a supporting electrolyte than $TBAClO_4$. Additionally, the thioacetate-EDOT monomer yielded better electrochemical performance than direct thiol-EDOT polymerization. Mechanical tests confirmed that this new thiolated interlayer significantly improved adhesion to the gold substrate.

The final dual-layer devices (Au/PEDOT-SAc/PEDOT:PSS) exhibited excellent electrochemical properties, including low impedance, a high electroactive area and good long-term stability.

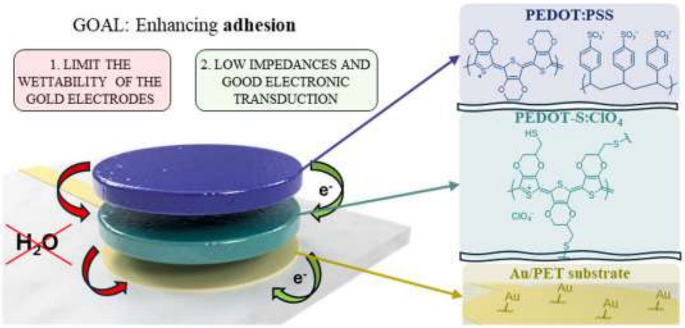

***Figure 1.*** Scheme of implantable conducting device.

**Keywords:** Adhesion, PEDOT:PSS, Electropolymerization, Implantable devices.

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# Morphology, crystallization and thermal properties of biodegradable and double crystalline poly(7-hydroxybutyrate)-*b*-poly(lactide) diblock copolymers

Arianna Cimino, Ricardo Arpad Pérez-Camargo, Bingzheng Huang, Yongzheng Li, Zhibo Li, Alejandro J. Müller.

*Student Name:* Arianna Teresa Cimino
*PhD programme:* Applied Chemistry and Polymeric Materials
*Laboratory Group Name:* Alejandro J. Müller's group
*Year of enrolment:* ■ *1st Year* □ *2nd Year* □ *3rd Year and more*

Novel biodegradable poly(7-hydroxybutyrate)-*b*-poly(lactide) (P7HB-*b*-PLA) diblock copolymers were synthesized with 15 and 85 wt% PLA, along with PLA ($M_n \approx 20$ kDa) and P7HB ($M_n \approx 3.7–21.5$ kDa). The crystallization behavior of both blocks was studied via non-isothermal and isothermal differential scanning calorimetry (DSC), including self-nucleation (SN) and Successive Self-nucleation and Annealing (SSA), with PLOM and WAXS/SAXS analyses.

Isothermal PLOM observations showed negative spherulites for PLA and P7HB, with P7HB morphology unaffected by molecular weight. PLA-rich copolymer exhibited slower spherulitic growth compared to neat PLA, and a non-banded spherulitic morphology. In contrast, P7HB-rich copolymer, formed banded spherulites, with spacing increasing with crystallization temperature due to lamellar twisting.

DSC under non-isothermal conditions showed P7HB transitions depend on molecular weight, reaching a plateau at high values, while PLA transitions were consistent with literature reports. Isothermal DSC [1] demonstrated that the P7HB crystallization rate increases with molecular weight but decreases in the presence of PLA.

SN experiments [2] identify three self-nucleation domains for both polymers. PLA exhibits a wider melt memory region (*Domain IIa*) due to stronger intermolecular interactions, whereas P7HB did not show melt memory but only self-seeding (*Domain IIb*), due to its long chain length, which resembles that of polyethylene. Ongoing SSA and temperature-dependent WAXS/SAXS studies aim to clarify microstructure and phase organization.

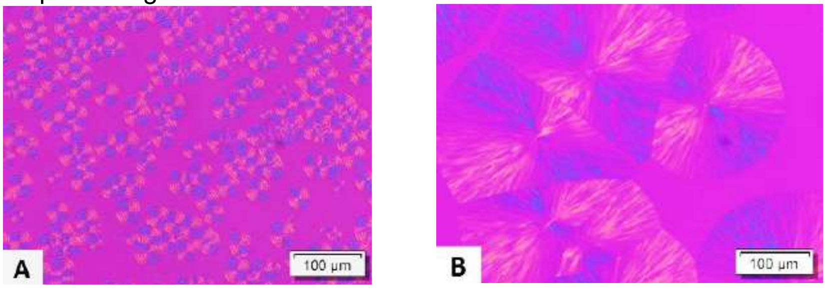

***Figure 1.*** *PLOM micrographs under isothermal crystallization: (A) P7HB-rich copolymer at 53ºC, showing banded spherulites; B) PLA-rich copolymer at 110ºC, showing spherulitic morphology.*

**Keywords:** PLA block copolymers, crystallization kinetics, spherulitic morphology, SSA.

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# The next level of sustainability in emulsion polymerization

Luana Caroline de Oliveira Lima, Maria Paulis Lumbreras.

*Student Name: Luana Caroline de Oliveira Lima*
*PhD program: Applied Chemistry and Polymeric Materials*
*Laboratory Group Name: Polymerization Processes (POLYMAT)*
*Year of enrolment:* ■ *1st Year* ☐ *2nd Year* ☐ *3rd Year and more*

Emulsion polymerization is widely recognized as a sustainable technology due to its use of water as reaction medium and its critical role in enabling the transition from solventborne to waterborne coatings. However, the process typically operates at 60–80 °C, requiring substantial thermal energy, even though free radical polymerization is intrinsically exothermic. Lowering the reaction temperature represents a practical strategy to reduce energy consumption and improve process sustainability.[1]

To address this, the present preliminary work investigates redox initiation systems capable of promoting emulsion polymerization at temperatures ≤ 50 °C. To this end, potassium persulfate/sodium bisulphite (KPS/SBS) as well as ammonium persulfate/sodium bisulphite (APS/SBS) were chosen to evaluate their efficiency on a MMA/BA/MAA model system. A seed polymerization was conducted at 80°C using KPS, followed by seeded semibatch reactions at 30, 40, and 50 °C. Two different feeding strategies for the redox components were applied to assess their impact on radical generation and reaction control.[2,3]

The results indicate that both temperature and redox addition strategy significantly affect monomer conversion and reaction kinetics. Additionally, characterizations such as gel content, molecular weight distribution, and water uptake have been taken to evaluate whether temperature and initiator system compromise material performance.

**Keywords:** redox systems; low-temperature polymerization; energy efficiency

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# Studying The Organization Of Collagen Fibers In Engineered Bioprinted Materials Using SHG-microscopy and SAXS.

Guilherme H. Oliveira[1,2], André L. C. Conceiçao[3], Giuseppe Chirico[2], Carlos Sanchez-Cano[1,4,5]

[1] Donostia International Physics Center, Donostia, 20018, Spain
[2] Department of Physics, Università di Milano-Bicocca, Milan, 20126, Italy
[3] Deutsches Elektronen-Synchrotron DESY, Hamburg, 22607, Germany
[4] Ikerbasque, Basque Foundation for Science, Bilbao, 48011, Spain
[5] Polimero eta Material Aurreratuak: Fisika, Kimika eta Teknologia, Kimika Fakultatea, Euskal Herriko Unibertsitatea UPV/EHU, Donostia, 20018, Spain

Student Name: *Guilherme Henrique de Oliveira*
PhD programme: *Química Aplicada y Materiales Poliméricos*
Laboratory Group Name: *XInorgBio: X-rays for Inorganic Biochemistry*
*Year of enrolment:* *2st Year*

Collagen is the most abundant protein in mammals and the main structural component of connective tissues, responsible for the function and mechanical properties of several organs. Consequently, alterations in collagen organization contribute to pathological conditions such as fibrosis[1]. Collagen is also a key building block for many scaffolds used to generate synthetic tissues by bioprinting. Therefore, probing the structural properties and spatial arrangement of this protein is crucial both to understand the mechanism of diseases and optimize the characteristics of biomaterials.

Second Harmonic Generation (SHG)[2] microscopy and Small-Angle X-ray Scattering (SAXS)[3] offer complementary insights into collagen architecture, providing microscale, label-free imaging and nanoscale structural quantification, respectively. This project aims to optimize a correlative SHG-SAXS workflow to probe dynamic systems with SHG and analyze selected time points with higher-resolution SAXS.

We have developed a mesoscopic anisotropy metric (Equation 1) that quantifies angular dispersion of collagen fibers, enabling automated assessment of pore size distribution and preferred fiber orientation and its distribution.

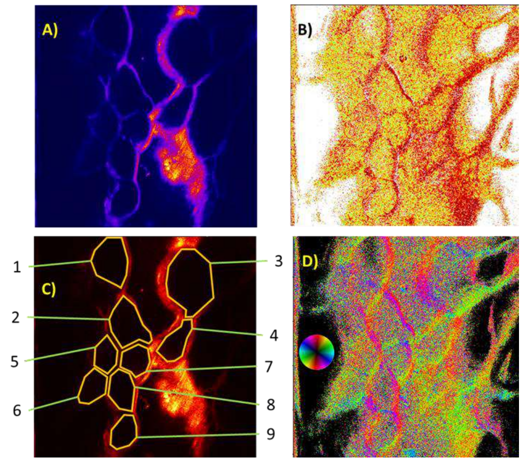

**Figure 1**. Collagen fibers images 525x525 μm2, collected by SHG-microscopy technique **A)** Raw image collected in an arbitray polarization angle. **B)** The treated image, showing the meso-anysotropy using equation 1. **C)** Evaluation of Pore size distribution and **D)** image treated showing the main orientation per pixel.

Using this workflow, we are investigating how bioprinting parameters, such as needle gauge, extrusion pressure, collagen concentration, and the presence of fibroblasts cells, could affect collagen fiber organization and the material structure and properties. Data acquisition is ongoing, and preliminary results demonstrate the potential of this combined method to characterize structural changes induced by bioprinting conditions.

$$\gamma_k = 1 - \frac{4}{N\pi^2}\sum_{i=1}^{N}(\theta_i - \theta_k)^2 \rightarrow \quad 0 \leq (\theta_i - \theta_k) \leq \frac{\pi}{2}, \qquad 0 \leq \gamma_k \leq 1 \qquad (eq.1)$$

**Keywords:** SHG, SAXS, Collagen, Fiber Orientation, Anisotropy, Python

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# Synthesis of biodegradable copolyesters from monomers that can be derived from biomass: Characterization and Application

Marta Elorza Romero1, Md Shafi Alam[1], Agustín Etxeberria Lizarraga[1], Ainara Sangroniz Agudo[1]
[1]POLYMAT and Department of Polymers and Advanced Materials: Physics, Chemistry and Technology, Faculty of Chemistry, University of the Basque Country UPV/EHU, 20018 Donostia-San Sebastian, Spain;

*Student Name: Marta Elorza*
*PhD programme: Master student of Chemistry and Polymers*
*Laboratory Group Name: Sangroniz Lab (Polymat)*
*Year of enrolment: ☐ 1st Year ☐ 2nd Year ☐ 3rd Year and more*

Plastic packaging is essential to protect the food and ensure its quality and safety. However, the plastics employed nowadays in the market are not sustainable, they are obtained from oil and since they are not easy to recycle or biodegradable, once disposed they contribute to the issue of plastic waste. Bearing this in mind, in this work, the synthesis of biobased polyesters are targeted which show high potential for the packaging sector. As monomers, 1,5-pentanediol (1,5-PDO), succinic acid (SA) and furan dicarboxylic acid (FDCA) have been used, all of which are compounds of renewable origin. The main objective of the project is the development of a biobased and potentially biodegradable polymer and its application in the packaging sector as a sustainable alternative.

The synthesis was carried out by polycondensations and several copolymers were synthetized by varying the molar ratios of succinic acid and FDCA to evaluate how the composition affects the final properties of the polymer. The products obtained were characterized by analysing the thermal properties by DSC (Differential Scanning Calorimetry), GPC (Gel Permeation Chromatography) to determine molecular weight; FTIR (Fourier Transform Infrared Spectroscopy) to identify the functional structures of the polymer and the carbon-13 NMR ($^{13}$C-NMR) and proton NMR ($^{1}$H-NMR), to verify the chemical structure of the polymer and its composition. Finally, with the aim to analyze the suitability of the materials in the packaging sector the permeability to oxygen and water vapour was analyzed.

**Keywords:** Biodegradable polymer, polyester, packaging.

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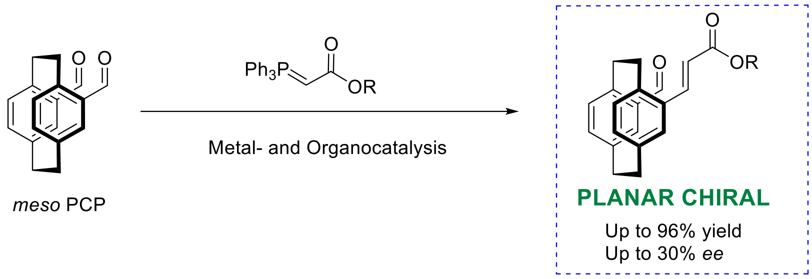
# Desymmetrization of [2,2]Paracyclophanes via the Wittig reaction

Héctor E. Fernández; Rosa López; Enrique Gómez-Bengoa

*Student Name: Héctor Elpidio Fernández Pascual*
*PhD programme: Synthetic and Industrial Chemistry*
*Laboratory Group Name: Dept. Organic Chemistry I*
*Year of enrolment: 2nd Year*

The rigidity of [2,2]paracyclophanes (PCPs) have enabled their use in a wide range of chemistry areas, such as hole-transport systems, chiral ligands/catalysts, MOFs, …, attracting increasing interest.[1,2] Despite the growing interest, the stereoselective preparation of PCPs is still challenging, as access to enantiomerically pure PCPs mostly depends on chromatographic resolution.[3] To contribute to the diversity of methodologies, we are exploring an underveloped but yet promising synthetic area: the catalytic asymmetric carbon–carbon double bond formation via selective differentiation of *meso* disubstituted [2,2]PCP.[4] Here we present our efforts towards enantioselective metal- and organocatalyzed Wittig olefinations. By exploiting the steric hindrance present in the pseudo-geminal PCPs, we have been able to control monofunctionalization versus difunctionalization, although the enantiomeric excess remains low.



Aknowledgements: We thank the Basque Government (EJ, grant IT1741-22) and Agencia Estatal de Investigación (grant PID2023-147050NB-I00//MCIU AEI/10.13039/501100011033) for financial support. H. E. F. acknowledges an FPI fellowship from MCIU.

**Keywords:** Paracyclophane, desymmetrization, planar chirality, olefination, Lewis Acid.

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# ABS material properties: Influence of thermal and mechanical aging

B.Ferrer-Diaz, A. Agirre, M. Perez, A. Prunera, M. Ximenis, H. Sardon

*Student Name: Beatriz Ferrer Diaz*
*PhD programme: Applied Chemistry and Polymers*
*Laboratory Group Name: Catalysis and Sustainable Polymers*
*Year of enrolment: ☐ 1st Year ■ 2nd Year ☐ 3rd Year and more*

Acrylonitrile-butadiene-styrene (ABS) is a widely used engineering thermoplastic in automotive, electronics, and consumer products.[1] Its heterogeneous structure, consisting of a styrene-acrylonitrile (SAN) matrix with dispersed polybutadiene domains, makes it highly sensitive to thermal, mechanical, and oxidative aging, which can significantly affect long-term performance and stability.[2]

This study characterizes ABS to evaluate its recyclability and establish a baseline of its material condition. Instead of optimizing recycling processes, the focus is on understanding the material's state and the factors that may influence future recycling strategies. Results show signs of aging and degradation, particularly linked to the polybutadiene phase, affecting overall material behavior and performance. Observed structure-property relationships highlight how microscopic changes influence macroscopic properties. These findings provide insight into ABS behavior during service and reprocessing, supporting a more informed assessment of its recyclability and offering a foundation for developing efficient and sustainable recycling approaches.

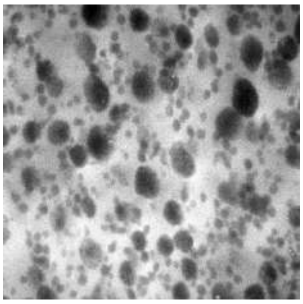

***Figure 1.*** *TEM image showing the SAN matrix and dispersed polybutadiene domains in ABS.*

**Keywords:** ABS, Degradation, Recyclability, Structure-property relationship

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# Exploration of Chiral Anionic Organobases as Catalysts for Enantioselective Synthesis of Chiral $\gamma$-Nitrosulfones

Iker Ferreras and Antonia Mielgo*

*Student Name: Iker Ferreras Martinez*
*PhD programme: Synthetic and Industrial Chemistry*
*Laboratory Group Name: Organic Chemistry I, Asymmetric Catalysis*
*Year of enrolment:* ☐ *1st Year* ✓ *2nd Year* ☐ *3rd Year and more*

The enantioselective synthesis of α-stereogenic nitro compounds remains an important objective due to the strategic value of the nitro group, which serves as a versatile precursor to chiral amines and other functional motifs of synthetic relevance. Despite significant advances, existing asymmetric approaches lack generality. In particular, the α-functionalization of secondary (α-branched) nitroalkanes is especially demanding and commonly depends on electron-withdrawing substituents to promote nitronate formation.[1] In contrast, our study addresses secondary nitroalkanes devoid of such activating groups (Figure 1), representing a more challenging and less explored substrate class.

Herein, we evaluate the efficiency of chiral bifunctional anionic organobases (almost unexplored in asymmetric catalysis) in the synthesis of $\gamma$-nitrosulfones from nitroalkanes and vinyl sulfones. To this end, a variety of ureates and thioureates were examined as catalysts, generated *in situ* from the corresponding ureas and thioureas (precatalysts) upon treatment with a suitable strong base. Importantly, these precatalysts do promote the reaction, affording excellent conversions and yields, although enantioselectivity still requires optimization. The best enantiomeric excess were obtained with bis(thio)ureas (type B) and amides (type D). The enantioselectivity values observed, although moderate, are among the highest observed for this type of bases. Further studies are currently underway.

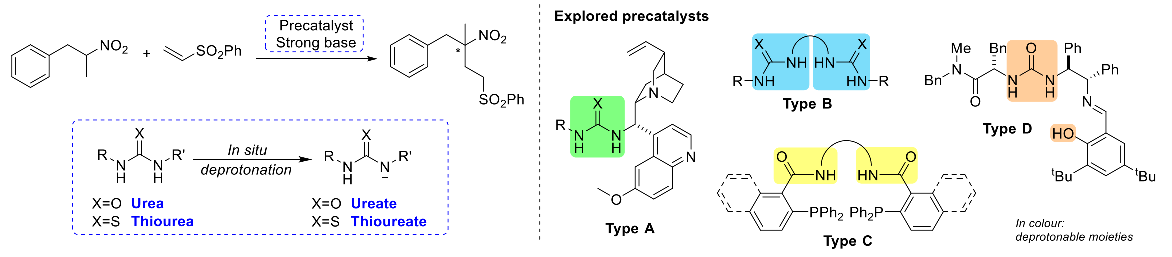

***Figure 1.** Chiral anionic organobases as catalysts en route to $\gamma$-nitrosulfones.*

**Keywords:** anionic organobases, nitrosulfones, (thio)ureates, asymmetric catalysis.

**Aknowledgements:** We thank Agencia Estatal de Investigación (PID2022-137153NB-C21/AEI/ 10.13039/ 501100011033) and Basque Government (IT-1583-22) for financial support. I. Ferreras also thanks EJ-GV for a predoctoral fellowship.

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# Synthesis of new molecular entities based on glycomimetics

Presenting Nerea Fuertes Cayón

*Student Name:* Nerea Fuertes Cayón
*PhD programme:* Química Aplicada y Materiales Poliméricos
*Laboratory Group Name:* Polimerbio, PolyBioPack
*Year of enrolment:  X 1st Year* ☐ *2nd Year* ☐ *3rd Year and more*

The increase in life expectancy and the resulting aging population represent a significant challenge for healthcare systems, being the development of new therapeutic strategies essential.[1,2] Consequently, the development of innovative glycodrugs based on C60 fullerene functionalized with carbohydrate structures was studied. C60 fullerene was selected as a molecular platform due to its high structural stability and its ability to neutralize reactive oxygen species, making it a promising scaffold for antioxidant and biomedical applications. The synthetic approach involved the preparation of malonate derivatives containing terminal alkyne and halogenated groups, which were subsequently used for the functionalization of the C60 fullerene. Through Click Chemistry, carbohydrates previously functionalized with azide groups were attached to the C60 fullerene. Using this methodology, six different C60-based structures functionalized with D-mannose were successfully synthesized (Figure 1).

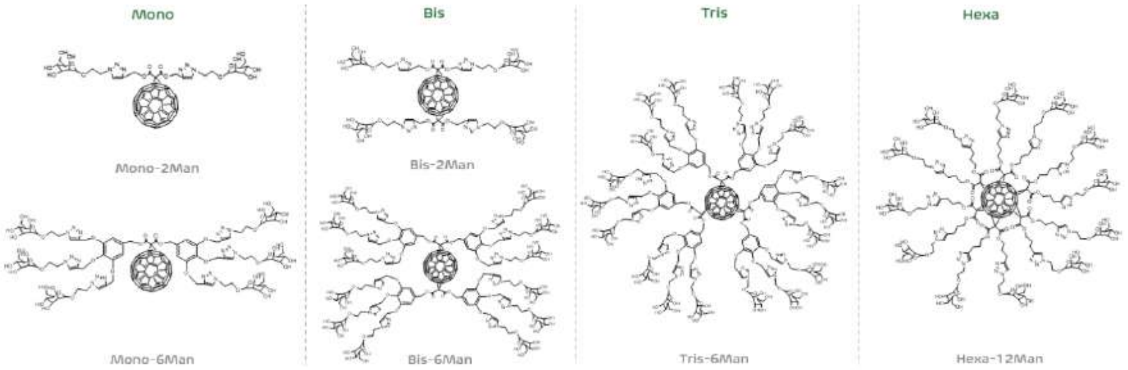

***Figure 1.** Structures of the synthesized C60 derivatives.*

The biological properties of the synthesized compounds were evaluated through cytotoxicity, antioxidant, and immunomodulatory assays. Cytotoxicity studies in human keratinocytes showed no toxicity at low concentrations, although Bis-2Man, Mono-6Man, and Tris-6Man presented cytotoxic effects at higher concentrations. Antioxidant assays demonstrated that some derivatives produced antioxidant effects comparable to those of ascorbic acid. In addition, immunomodulatory studies revealed no cytotoxicity up to 100 μM and identified Hexa-12Man and Bis-6Man as promising candidates, as they reduced both pro- and anti-inflammatory cytokine secretion. Additionally, all compounds displayed increased phototoxicity, suggesting potential applications in photosensitive therapies. Overall, the successful derivatization of C60 improved its solubility and generated compounds with promising antioxidant and immunomodulatory properties, highlighting their potential for therapeutic applications in inflammation-related conditions.

**Keywords:** C60 fullerene, glycodrugs, carbohydrates, *Click Chemistry*.

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# Mixed Ionic Electronic Conducting Polymers Based on PEDOT:PSS and Protic Organic Ionic Plastic Crystals

Paula García Foronda[1], Ilaria Abdel Aziz[1], Nerea Casado[1,2]

*[1]POLYMAT, University of the Basque Country, 20018 Donostia-San Sebastián, Guipuzkoa, Spain*
*[2]IKERBASQUE, Basque Foundation for Science, Bilbao 48011, Spain*

*Student Name:* Paula García Foronda
*PhD programme:* Química Aplicada y Materiales Poliméricos
*Laboratory Group Name:* Innovative Polymers Group
*Year of enrolment:* ☐ *1st Year* *x 2nd Year* ☐ *3rd Year and more*

Organic mixed Ionic Electronic Conductors (OMIECS) are polymers based on conducting polyelectrolyte that show both ionic and electronic conductivity. This type of materials is widely used in bioelectronics, electrochromic devices, robotics… as well as in batteries and fuel cells[1]. In fuel cells, these polymers are crucial for enhancing proton transport and catalyst utilization within the electrode layers, as they facilitate simultaneous proton transport and electron conduction. However, OMIECs that show specifically proton conductivity, rather than simple cationic one, have been studied to a little extent so far, despite the potential improvement especially for fuel cells applications.

Poly(3,4-ethylenedioxythiophene) (PEDOT) remains one of the most commonly used conducting polymers due to its commercial availability and excellent conductive properties[2]. Its polymer backbone carries an excess of positive charge, which is typically compensated by anions such as polystryrene sulfonate (PSS) to improve processability and water solubility. Numerous studies have focused on enhancing the conductive and mechanical properties of this dispersion, by secondary doping with ionic liquids and organic ionic plastic crystals (OIPCs).

Based on previous research[3], we present a variety of PEDOT:PSS mixtures with different protic OIPCs obtaining robust and homogeneous membranes. These materials were thoroughly characterized through chemical and electrochemical methods showing promising properties for next-generation electrochemical devices where both ionic and electronic conductivity are required.

**Keywords:** OMIECs, PEDOT:PSS, protic OIPC, electronic conductivity, electrolizers.

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# Strategies Towards the Late-Stage Bioconjugation of Tyr-Containing Peptides

Carlota Girón-Elola[1] and Arkaitz Correa[1]

[1] University of the Basque Country (UPV/EHU), Department of Organic Chemistry I, Joxe Mari Korta R&D Center, Avda. Tolosa 72, 20018 Donostia-San Sebastián (Spain)

*Student Name: Carlota Girón Elola*
*PhD programme: Química Sintética e Industrial*
*Laboratory Group Name: Catálisis Sostenible: Métodos y Computacional*
*Year of enrolment:* ☐ *1st Year* ☐ *2nd Year* ☒ *3rd Year and more*

Synthetically modified amino acids and peptides derived thereof are key building blocks in the field of proteomics, drug discovery and chemical biology owing to their often-enhanced biological activities and drug-like physicochemical properties.[1] Therefore, the development of methodologies for the late-stage tagging of such biomolecules remains a priority in the organic and medicinal chemistry areas.[2] In line with our work on metal-catalyzed late-stage C–H functionalization,[3] our group has developed several strategies for the selective bioconjugation of tyrosine (Tyr),[4] a privileged phenol-containing amino acid widely found in bioactive peptides and proteins. This contribution provides an overview of different methodologies enabling the regioselective *ortho*-functionalization of this amino acid, allowing the formation of synthetically and biologically relevant C–N,[5] C–S and C–C[3b] bonds. Mechanistic aspects of these protocols are also discussed, which rely either on the installation of an external directing group (DG) or on exploiting the innate electronic reactivity of the phenol ring, enabling the selective functionalization of native peptides.

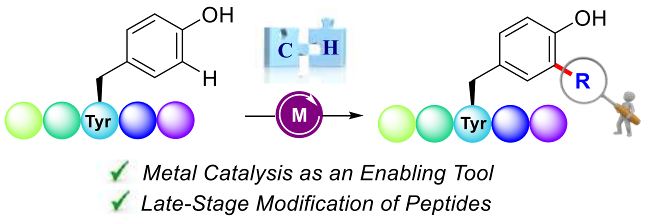

***Figure 1.** Site-selective late-stage functionalization of Tyr-based peptides*

**Keywords:** Late-stage functionalization, amino acids, peptides, tyrosine.

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# The Influence of Composition and Coupling Approaches on g-$C_3N_4$/PEDOT:PSS Hybrid Thin Films

M. Guerra[1,2], J. Gutierrez[1], A. Tercjak[1], E. San Sebastian[2]

*Student Name:* Maialen Guerra Mantzizidor
*PhD programme:* Applied Chemistry and Polymeric Materials
*Laboratory Group Name:* [1]Group `Materials + Technologies´ (GMT), Dept. of Chemical and Environmental Engineering, Faculty of Engineering, Gipuzkoa, and [2]Dept. of Applied Chemistry, Faculty of Chemistry, University of the Basque Country (UPV/EHU)
*Year of enrolment:* ☐ *1st Year* X *2nd Year* ☐ *3rd Year and more*

Hybrid materials based on conductive polymers and visible-light-active semiconductors offer promising pathways for enhancing optoelectronic performance. In this work, we investigated spin-coated multilayer PEDOT:PSS thin films modified with graphitic carbon nitride (g-$C_3N_4$), synthesised via pyrolysis of melamine. We further investigate how composition and interfacial coupling influence their structural and optoelectronic properties.

Hybrid films were prepared playing with different g-$C_3N_4$/PEDOT:PSS ratios and employing two different strategies: mixed and multilayer systems. Surface morphology and distribution of g-$C_3N_4$ nanosheets was investigated by means of AFM and UV-Vis spectroscopy was used to estimate the band gap of developed systems.

Chopped-light chronoamperometry clearly showed that the incorporation of g-$C_3N_4$ nanosheets increase the photoconductivity of the films, as evidenced by the higher photo-induced current and the efficient charge-separation processes. Among the different studied strategies, the multilayer films exhibited the strongest photoresponse. Furthermore, these measurements confirmed the good stability of the hybrid films under aqueous conditions throughout repeated illumination cycles.

**Keywords:** PEDOT:PSS; g-$C_3N_4$ nanosheets; thin films; photoconductivity

## Acknowledgements

This work was supported by the Basque Government (Eusko Jaurlaritza) through the Elkartek Programme via projects ELKARTEK25/21 (KK-2025/00022) and ELKARTEK21/36 (KK-2021/00009), and through the Grupos Consolidados Programme (IT-1690-22). M. G. M. also acknowledges support her predoctoral contract PIF25/253 from the University of the Basque Country (UPV/EHU).

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# Balancing Adhesion and Cohesion in High Bio-Content Itaconate-Based Waterborne Pressure-Sensitive Adhesives Reinforced with Cellulose Nanocrystals

Jyoti Gupta, Miren Aguirre and Radmila Tomovska

Student Name: Jyoti Gupta
PhD programme: Industrial Liaison Program
*Laboratory Group Name:* Polymerization Processes Group
Year of enrolment: ☐ 1st Year ☐ 2nd Year ☒ 3rd Year and more

Novel waterborne biobased pressure-sensitive adhesives (PSAs) with bio-contents ranging from 28–78% were synthesized via the copolymerisation of fully biobased dibutyl itaconate (DBI) with partially biobased monomers, including 2-octyl acrylate (2-OA), isobornyl acrylate (IBOA), and isobornyl methacrylate (IBOMA). For comparison, conventional monomers such as methyl methacrylate (MMA) and butyl acrylate (BA) were also employed. All polymers were produced through emulsion polymerizatiom an environmentally friendly approach that enables precise control over copolymer microstructure while significantly reducing volatile organic compound (VOC) emissions in the final adhesive formulations.In addition, sulphate cellulose nanocrystals (sCNCs) were investigated as performance-enhancing modifiers to address the inherent adhesion cohesion trade-off in PSAs by simultaneously improving interfacial bonding and internal strength. Stable nanocomposite latexes, based on both biobased and conventional systems, were successfully prepared by blending sCNCs at loadings between 0.25 and 1 phm relative to monomer weight. The resulting PSA films exhibited systematic improvements in shear strength, tack, and peel strength with increasing sCNC content, while also significantly increasing the overall biobased content.To the best of our knowledge, this work represents the first study incorporating sCNCs into fully biobased PSA formulations, as prior research has predominantly focused on conventional monomer systems. This approach not only enhances adhesive performance but also establishes a promising pathway toward durable, high-biocontent nanocomposite PSAs with long term application potential.

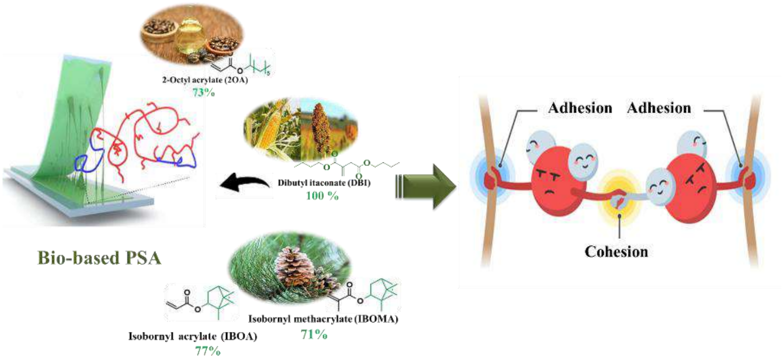


**Figure 1**: Graphical abstract

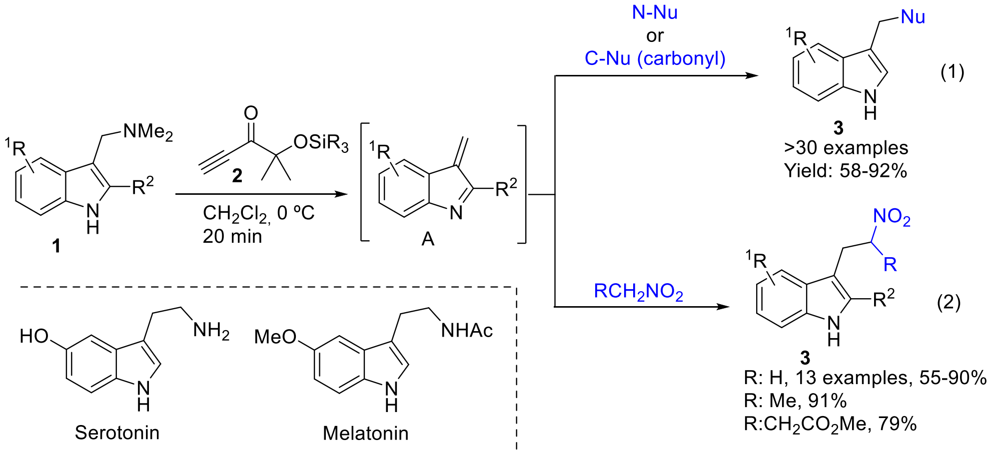
# Ynone-Promoted Coupling of Nitromethane to Gramines

I. Gurrutxaga,[a] G. Dominguez,[a] A. Landa,[a] M. Oiarbide[a]

*Student Name: Iker Gurrutxaga Cardenal. <igurrutxaga019@ikasle.ehu.eus>*
*Synthetic and Industrial Chemistry MSc Student*
*Laboratory Group Name: [a]Department of Organic Chemistry I, Universidad del País Vasco UPV/EHU*

The deaminative coupling of gramines with diverse nucleophiles upon prior C-N bond activation offers access to a wide range of compounds bearing the (1*H*-indole-3-yl)methyl fragment.[1] Among the diverse activation approaches, simple acetylene esters (e.g. acetylenedicarboxylate or ethyl propiolate) have been shown capable of mild C-N bond activation, presumably through N-quaternization *via* the aza-Michael reaction.[2] However, yields are generally modest and the nucleophile scope limited. Recently, we have explored alternative acetylenic reagents **2** that have shown to be powerful activating reagents in reactions involving C-centered (mainly enolizable carbonyl compounds) and N-centered nucleophiles (Scheme 1, equation 1).[3]

In this communication we demonstrate that nitroalkanes, focusing particularly on nitromethane, also engage efficiently in the alkyne-promoted coupling with gramines, giving rise to 3-(2-nitroethyl)-1H-indole derivatives (Scheme 1, equation 2). These adducts represent precursors for interesting amino compounds such as neurotransmitter serotonin or hormone melatonin.



***Scheme 1.*** *Graphical summary of this work.*

**Keywords:** *Gramines, C-N bond activation, ynones, nitro compounds.*

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# Single chain nanoparticles for applications in nanomedicine

Sara Gutiérrez Lkourt

*Student Name:* ***Sara Gutiérrez Lkourt***
*PhD programme:* ***Physics of Nanostructures and Advanced Materials***
*Laboratory Group Name:* ***Polymers and soft matter group (CFM)***
*Year of enrolment:* ***X*** *1st Year* ☐ *2nd Year* ☐ *3rd Year and more*

Single Chain Nanoparticles (SCNPs) are nanomaterials formed by the intramolecular folding of individual polymer chains, generating structures with internal compartments and high flexibility. Their small size and ability to form hydrophobic cavities make them promising for biomedical applications, including drug delivery, imaging, and targeted therapies. However, the mechanisms governing medium-dependent folding and interactions with biomimetic membranes are not yet fully understood, limiting the rational design of functional nanocarriers. [1-2]

This work aims to develop SCNPs as smart nanocarriers for encapsulating highly hydrophobic antitumor compounds, particularly those active against cholangiocarcinoma, whose clinical use is limited by poor solubility. Inspired by biological systems, random amphiphilic and bioinspired copolymers containing phosphorylcholine groups (MPC) and acetoacetoxyethyl methacrylate (AAEMA) were synthesized via RAFT photopolymerization, promoting controlled folding, biocompatibility, protein resistance, and water solubility.

Their interaction with, 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) biomimetic membranes is currently being evaluated to assess adsorption, insertion, and hydrophobic segment penetration. Preliminary results indicate that interaction is enhanced in the presence of calcium ions. Complementary techniques (SAXS, AFM, and dye labeling) are being implemented to determine folding efficiency and the extent of membrane penetration.

These developments contribute to the rational design of bioinspired SCNPs capable of improving the solubility and delivery of hydrophobic drugs, laying the groundwork for their application in advanced therapies against cholangiocarcinoma and other hard-to-treat cancers.

**Keywords:** Single Chain Nanoparticles, biomimetic membranes, drug delivery, cholangiocarcinoma

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# Delivery and Activation of Organometallic Anticancer drugs using Ionic Liquids

L. Hernandez-Fernandez, M. Costa, E. Formoso, L. Salassa, E. Rezabal

*Student Name: Laura Hernández Fernández*
*PhD programme:  Theoretical Chemistry and Computational Modeling*
*Laboratory Group Name: Polymers and Advanced Materials: Physics, Chemistry and Technology*
*Year of enrolment:* ■ *1st Year* □ *2nd Year* □ *3rd Year and more*

Choline-based Deep Eutectic Solvents (DESs) and Ionic Liquids (ILs) are environmentally sustainable and cost-effective solvents with applications ranging from biomass processing to transdermal drug delivery. Among them, choline geranate (CAGE) stands out due to its high biocompatibility and antimicrobial properties, making it a promising candidate for medical applications such as drug delivery [1]. However, its molecular interactions and its influence on the physicochemical properties and reactivity of delivered drugs remain poorly understood. We hypothesize that CAGE not only acts as a delivery medium but may also induce new reactivities or modulate existing ones.

In this work, we investigate the delivery and activation of Pt(IV) and Ru complexes with anticancer properties. First, we examine the solvation pattern of a Pt(IV) anticancer prodrug in CAGE to understand its delivery and potential conversion into the active Pt(II) species in biological environments. This study combines force-field molecular dynamics simulations with density functional theory (DFT) calculations.

We also explore the activation of the Ru polypyridyl complex $(Ru(bpy)_3)^{2+}$, focusing on ligand photorelease through excited states and evaluating the energetic and structural changes induced by photoactivation using DFT calculations [2].

**Keywords:** Computational, DFT, MD, Ionic Liquids, Deep Eutectic Solvent.

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# Dry & Wet Processed Gel-Polymer Electrolytes and Cathodes

P. Imaz-Elizalde, L. Fernandez-Diaz, J. Blanco, M. Armand, A. Villaverde, M.C. Morant-Miñana

*Student Name: Paul Imaz Elizalde*
*PhD programme: Applied Chemistry and Polymeric Materials*
*Laboratory Group Name: Solid-State Microstructures (CIC energiGUNE)*
*Year of enrolment:* ■ *1st Year* ☐ *2nd Year* ☐ *3rd Year and more*

Gel-polymer solid-state batteries have emerged as one of the most promising alternatives in electrochemical energy storage. These innovative batteries consist of a lithium metal anode, along with a gel-polymer electrolyte and cathode, where the polymer matrix encapsulates a liquid electrolyte, giving the system a quasi-solid consistency.[1] While offering advantages such as excellent ionic conductivity at room temperature and mechanical stability, this technology faces several processing challenges, particularly the use of organic solvents in wet processing.[2] Therefore, a key challenge is transitioning to solvent-free processing methods to reduce costs and eliminate the use of toxic solvents without losing performance.

The primary goal of this PhD project is to develop gel-polymer electrolytes and cathodes using dry & wet processing techniques. The gel-polymer electrolyte will be processed with a torque mixer, and the effects of processing conditions (e.g., mixing time and speed) and formulation parameters (e.g., plasticizer percentage and component ratios) on the final material will be studied. Characterization will include ionic conductivity, thermal analysis, and FTIR. Additionally, an improved gel-polymer cathode, with optimized formulation and solid content, will be produced via wet processing as a reference,[3] and characterized using SEM, resistivity measurements and ionic conductivity tests.

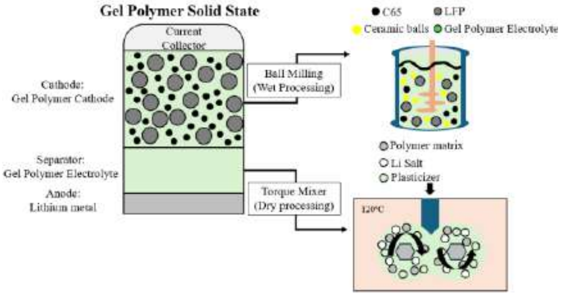

***Figure 1.*** *Gel-polymer Solid State Battery scheme*

**Keywords:** Gel-Polymer Electrolyte, Jellified Cathode, Electrode Manufacturing, Lithium Metal Batteries, Solid-State Batteries

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# Development of semicrystalline sustainable polymers

Chetan Jagtap, Leire Sangroniz

*Student Name: Chetan Jagtap*
*PhD programme: Applied Chemistry and Polymeric Materials*
*Laboratory Group Name: Alejandro Muller's Group*
*Year of enrolment: ☐ 1st Year ☐ 2nd Year ☐ 3rd Year and more*

Polymer have unique properties such as low density, durability, and low production cost. However, after a short period of time they are discarded contributing to the plastic waste issue. The 75 % of the polymers in the market are semicrystalline, those are obtained mainly from petroleum based sources and can not be biodegraded or chemically recycled. To overcome this issue, we have developed a sustainable polymer system. We have synthetized poly(pentamethylene furanoate) (PPeF) by using the 2,5-furandicarboxylic acid which is a biobased organic compound. Although this polymer displays interesting properties, it has low crystallinity which limits its application. To enhance crystallinity, we introduce several nucleating agents such as talc or orotic acid. The impact of the nucleating agents on the thermal, structure and morphological properties of poly(pentamethylene furanoate) (PPeF) have been investigated. Polymer films of neat polymer and polymer/nucleating agent (1 wt %) were prepared via solvent casting. Differential Scanning Calorimetry (DSC) reveals that nucleating agent induces crystallization. Polarized Optical Microscopy (PLOM) and FT-IR spectroscopy provide insights into morphological changes and molecular interactions. These findings offer valuable guidance for tailoring biodegradable polymers and widening their applications.

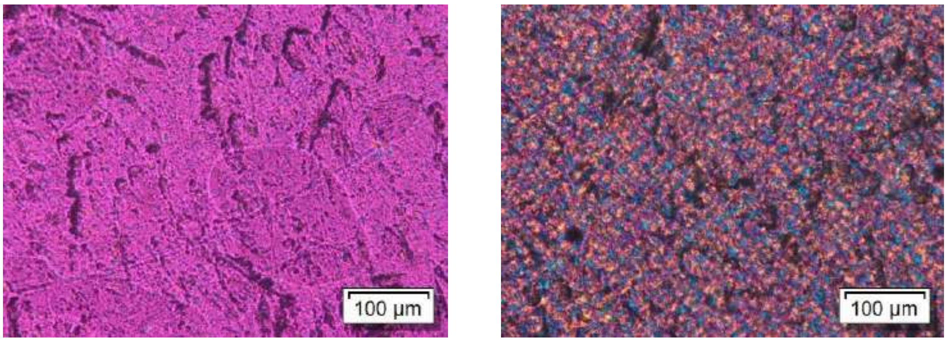

***Figure 1.*** *PLOM photographs of poly(pentamethylene furanoate) (PPeF) and PPeF/talc at room temperature.*

**Keywords:** Polymer, sustainable, crystallization.

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# Unseen Forces: The Overlooked Role of Flow Conditions in Polyelectrolyte Multilayer Formation and Their Impact on Membrane Pore Modification

Kaja Kogal[1,2], Thomas Schäfer[1,2,3]
[1]POLYMAT and Advanced Polymers and Materials Department, University of the Basque Country UPV/EHU, 20018 Donostia-San Sebastián, Spain
[2]SURPHASE, 20018 Donostia-San Sebastián, Spain
[3]IKERBASQUE, Basque Foundation for Science, Bilbao, Spain

*Student Name: Kaja Kogal*
*PhD program: Applied Chemistry and Polymeric Materials*
*Laboratory Group Name: NanoBioSeparations, and Surphase*
*Year of enrolment:* ☒ *1st Year* ☐ *2nd Year* ☐ *3rd Year and more*

Polyelectrolyte multilayers (PEMs) are nanostructured coatings formed by layer-by-layer assembly of oppositely charged polymers. While past studies focused on ionic strength, this work reveals that flow conditions have a much stronger impact than recognized.

Hydrodynamic condition effects were studied using two complementary techniques that provide real-time information on multilayer build-up, thickness, and kinetic data: surface plasmon resonance (SPR) and quartz crystal microbalance with dissipation monitoring (QCM-D). In previous work, we demonstrated high complementarity of the techniques for PEM formation on surfaces and porous membranes [1]. Polysodium 4-styrene sulfonate (PSS) and polydimethyl diallyl ammonium chloride (PDADMAC) were used at 0.15 M and 0.015 M NaCl. Water flux measurements were done on polyelectrolyte-modified polyethersulfone (PES) membranes.

When forming a five-layer PEM at 0.015 M NaCl, strong electrostatic interactions produced a dense multilayer about 4 nm thick, independent of flow rate (QCM-D and SPR). At a higher ionic strength, QCM-D showed a decrease in thickness from 14 nm to 6 nm with increasing flow, while SPR showed no change. This difference arises because QCM-D detects hydrated layers, whereas SPR measures only the polymer mass, indicating constant film thickness but reduced water content at higher flow rates.

PEMs assembly inside nanoporous PES membranes at varying flow rates shows that low flow causes a significant flux decrease, confirming formation of a thicker, more swollen multilayer.

Flow conditions must be carefully controlled during PEM formation. Depending on ionic strength, they influence PEM swelling, membrane performance, and reproducibility. Finally, we discuss the implications for PEM studies and recommend optimal flow conditions.

**Keywords:** Membrane modification, Polyelectrolyte multilayer, QCM-D, SPR

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# Innovative techniques to process polymer latexes: 3D printing

Jon Larrañaga, Miren Aguirre, Edurne Gonzalez

*Student Name: Jon Larrañaga Medinilla*
*PhD programme: Applied chemistry and polymeric materials*
*Laboratory Group Name: GIQ*
*Year of enrolment:* ***x 1st Year*** *☐ 2nd Year* *☐ 3rd Year and more*

Since the mid-20th century, polymer latexes have seen extensive industrial use due to their environmental benefits and processing versatility. Emulsion polymerization is the most common synthesis route. As aqueous dispersions of polymer particles, they allow for high molar masses and polymer concentrations without significantly increasing viscosity, as the latter depends primarily on particle number and size[1,2]. These unique characteristics make latexes highly attractive for Additive Manufacturing (AM), specifically for Vat Photopolymerization (VP). This independence between viscosity and molar mass enables the creation of complex geometries with excellent mechanical properties while significantly reducing waste[3]. Accordingly, the main objective of this project is to conduct a fundamental study on how latex properties influence VP. We are currently performing a thorough characterization of both commercial and laboratory-synthesized latexes by preparing specific formulations for printing. Preliminary results show that particle size, solids content, and pH directly impact system stability during the printing process. Furthermore, it has been demonstrated that post-printing chemical modifications can significantly enhance the final properties of the polymer.

***Figure 1.*** *Representation of Vat Photopolymerization*

**Keywords:** emulsion polymerization, latex, additive manufacturing, Vat photopolymerization

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# Bio-based polymer electrolytes for Li metal batteries

M. Larumbe, I. Villaluenga

*Student Name:* Mikel Larumbe
*PhD programme:* Doctorado en Química Aplicada y Materiales Poliméricos
*Laboratory Group Name:* Inorganic-polymer hybrid and nanostructured materials
*Year of enrolment:* ■ *1st Year* ☐ *2nd Year* ☐ *3rd Year and more*

In the framework of current environmental policies such as the 2030 Agenda, Europe is moving towards renewable energy sources, particularly wind and solar. Due to the intermittent nature of these energy sources the electrochemical energy storage systems (EESS) start playing a crucial role in enabling the use and storage of them. Among those systems, Li-ion batteries are the most studied and widespread since their commercialization in the 1990s. However, despite their technological maturity, limitations related to safety, flammability of liquid electrolytes and energy density motivate the exploration of alternative systems [1].

One of those promising next-generation technology is Li metal batteries due to the high theoretical volumetric capacity and low redox potential of lithium metal [2].

Solid-state electrolytes have emerged as a potential alternative to liquid electrolytes to improve safety and regulate lithium deposition. However, due to the intrinsic nature of solid materials, the ionic conductivity of these electrolytes is lower than the liquid ones. In this work, bio-based polymer membranes were developed. The materials were designed to combine mechanical stability with enhanced ionic transport properties.

The electrochemical properties have been characterized by Cyclic voltammetry (CV), Chronoamperometry and electrochemical impedance spectroscopy (EIS).

**Keywords:** Polymers, electrolyte, conductivity

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# Integrating Molecular Dynamics and ML for Predictive Modeling of iPPs

Héctor Lobato[1,3], Mikel Irigoyen[2], Unai Calvo[2], Jon M. Matxain[3,4], Aizeti Burgoa[1]

(1) LEARTIKER, (2) POLYMAT, (3) UPV/EHU, (4) DIPC

*Student Name: Héctor Lobato Basterra*
*PhD programme: Theoretical Chemistry and Computational Modelling*
*Laboratory Group Name: Kimika Teorikoa, POL-KT*
*Year of enrolment: 3rd Year and more*

As a sustainable alternative to traditional thermoset rubbers, thermoplastic vulcanizates (TPVs) successfully merge the elasticity of elastomers with the lightweight nature and processing ease of thermoplastics. However, accurately predicting the complex, non-linear behavior of TPVs requires a profound understanding of their continuous matrix, typically composed of isotactic polypropylene (iPP). Building on the proven efficacy of molecular dynamics (MD) in polymer mechanics [1, 2] and machine learning (ML) in materials science [3], this specific study focuses on establishing a robust MD-ML framework for predictive modeling.

Using LAMMPS, an extensive stress-strain database was generated for five iPP resins with distinct molecular weight distributions. The foundational phase of this workflow modeled amorphous iPP across diverse strain rates and system densities. Building upon this, the methodology is currently expanding to incorporate varying degrees of crystallinity to capture a more comprehensive spectrum of morphological states. To map these evolving microstructural features to their mechanical responses, algorithms ranging from interpretable Decision Trees to “black-box” Artificial Neural Networks—increasingly utilized for their capacity to capture intricate polymer behaviors [4]—were trained. A rigorous validation strategy—utilizing nested cross-validation, automated hyperparameter tuning, and group-splitting—ensured reliable generalization to unseen resins, while SHAP analysis elucidated the structural drivers of mechanical behavior.

Provisional results indicate that interpretable tree-based architectures achieve predictive accuracy comparable to neural networks with significantly less overfitting. Ultimately, this workflow facilitates the inverse design of the iPP matrix, establishing the groundwork to integrate rubber particle interactions and tailor the performance of complete TPVs.

**Keywords:** polymers, molecular dynamics, machine learning, mechanical properties, inverse design

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# *Designing poly (butylene succinate)/poly (butylene adipate-co-terephtalate)/poly (lactic acid) blends for Material Extrusion Additive Manufacturing*

Pablo López Matanza, Ricardo A. Pérez-Camargo, Nora Aranburu, Itziar Otaegi, Manuela Zubitur, Agurtzane Mugica, Supakij Suttiruengwong, Alejandro J. Müller

*Student Name: Pablo López Matanza*
*PhD programme: Applied Chemistry and polymeric materials*
*Laboratory Group Name: Thermal Analysis*
*Year of enrolment:* ☐ *1st Year* ☐ *2nd Year* ☐ *3rd Year and more*

This study investigates the printability of ternary polymer blends made of poly(butylene succinate) (PBS), poly(butylene adipate-co-terephthalate) (PBAT), and poly(lactic acid) (PLA) using fused filament fabrication (FFF). Biodegradable PBS is very difficult to print by FFF due to excessive warping arising from the high crystallinity developed during cooling from the melt; thus, a blending approach has been used to 3D print PBS-based materials. To establish a method for producing PBS-rich biodegradable materials, ternary blends were prepared with different PBS contents (20%, 40%, and 60%) while keeping a 1:1 ratio of PBAT to PLA. The blends were thoroughly analyzed with differential scanning calorimetry (DSC), polarized light optical microscopy (PLOM), and synchrotron radiation X-ray techniques to understand how crystallization affects the printing process. The results indicate that PBS nucleation is enhanced by PLA and PBAT, resulting in a refined morphology that significantly improves the mechanical performance of the printed parts. Printing conditions were optimized to successfully produce parts from these blends, followed by detailed testing of their mechanical properties. The printed blends exhibit yield stresses equal to or higher than those of their injection-molded counterparts, together with a highly ductile behavior compared to neat PLA. Notably, blends containing up to 60% PBS were successfully printed, showing excellent mechanical properties, with warping values below 1% and high ductility. Our approach led to the development of printable PBS-rich blends with enhanced mechanical and thermal properties, as well as significantly reduced warping, offering competitive features suitable for additive manufacturing of biodegradable semi-crystalline blends.

**Keywords:** Fused filament fabrication; Warping; PBS (Polybutylene succinate); PLA (Polylactic acid); PBAT (Polybutylene adipate-co-terephthalate).

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# Morphology driven Performance Improvement of Waterborne Pressure-Sensitive Adhesives

Marc Frederic Malter, Prof. José R. Leiza, Prof. María Paulis

*Student Name: Marc Frederic Malter*
*PhD programme: Applied Chemistry and Polymers*
*Laboratory Group Name: Polymerization Engineering and Simulation*
*Year of enrolment: ☐ 1st Year ☐ 2nd Year X 3rd Year and more*

Pressure-sensitive adhesives (PSAs) are widely used in packaging, automotive, healthcare, and electronics due to their ability to bond substrates under light pressure without heat or solvent activation. Their performance is governed by a balance of tack, peel adhesion, and shear strength, which strongly depends on polymer architecture and film morphology. In particular, waterborne acrylic PSAs are attractive because of their low volatile organic compound (VOC) emissions and environmental compatibility. However, their comparatively lower tack and adhesion, relative to solvent-based systems, require targeted structural optimization.

In this work, a morphology-driven design approach was employed to enhance the performance of reference waterborne acrylic PSAs. On one hand ASRs with high glass transition temperatures (Tg) were included to the reference PSA in order to promote the formation of controlled core–shell-like nanostructures within the polymeric matrix. On the other hand, an in situ synthesized tackifier was incorporated to investigate its influence on interfacial interactions and mechanical performance.

The resulting materials were comprehensively characterized in terms of adhesive performance, rheological behavior, and nanoscale morphology. Atomic force microscopy (AFM) provided detailed insight into phase distribution and structural organization at the nanometer scale. The combined control of the Tg and morphology, together with ASR and tackifier integration, demonstrates an effective strategy for improving the adhesion properties of waterborne acrylic PSAs while maintaining their environmental advantages.

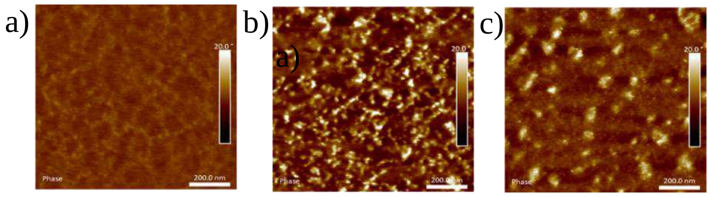

***Figure 1.*** *Schematic overview of the three morphologies: soft latex reference (compliant network), hard ASR formulation (rigid percolated structure), and in situ tackifier-modified system (phase-structured morphology).*

**Keywords:** Pressure-sensitive adhesive, emulsion polymerization, morphology, performance

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# NIPU/epoxy hybrid polymers based on carbonated soybean oil (CSBO): the influence of covalent adaptable networks (CAN) on reprocessability

Nahikari Martin-Larrañaga, Iker Razquin, Itziar Otaegi, Alba González, Lourdes Irusta

*Student Name: Nahikari Martin Larrañaga*
*PhD programme: Applied Chemistry and Polymers*
*Laboratory Group Name: Sustainable polymeric materials for advanced applications*
*Year of enrolment: ☐ **1st Year** ☐ 2nd Year ☐ 3rd Year and more*

Polymers are essential materials due to the wide range of properties and uses they offer. However, their recycling and reprocessing are significantly limited, especially regarding thermosetting polymers, because of the 3D network they exhibit. To address this problem, materials containing Covalent Adaptable Networks (CANs) have been developed. These materials are cross-linked polymers that behave as a bridge between thermoplastic and thermosetting materials [1]. They contain dynamic covalent bonds that can be activated by an external stimulus, which can facilitate and enable the reprocessability of these materials.

This work focuses on non-isocyanate polyurethanes (NIPUs) based on carbonated soybean oil (CSBO). Specifically, the reprocessing of different formulations of NIPU/epoxy hybrid polymers has been analyzed, as well as the physicochemical properties they exhibit. To synthesize these sustainable NIPU/epoxy hybrids, epoxidized soybean oil (ESBO) and carbon dioxide ($CO_2$) were used. The fixation of carbon dioxide was carried out through homogeneous catalysis in a high-pressure reactor (140 ºC and 30 bar) between soybean oil and $CO_2$ in the presence of a catalyst (3.5 mol% of CSBO) [2].

The reaction between the obtained CSBO, TMPTE (Trimethylolpropane triglycidyl ether) epoxy resin, and DAB (1,4-diaminobutane) diamine allows the synthesis of the aforementioned hybrid materials. The reprocessing of these hybrid materials was studied using via compression moulding. Furthermore, the properties of the resulting reprocessed materials were analysed using Young's modulus and DMA (Dynamic Mechanical Analysis) techniques, among others. Compared to the original material, the obtained material presented different properties suitable for use in coating or adhesive applications.

**Keywords:** Carbonated soybean oil (CSBO), NIPU/epoxy hybrid polymers, reprocessing, covalent adaptable network (CAN)

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# Synthesis of quantum dots based on novel materials for single photon light-sources

Anastasiia Murkina1, Gunnar Klös2, Aitziber L. Cortajarena3

Student Name: Anastasiia Murkina
PhD programme: Applied Chemistry and Polymeric Materials
Laboratory Group Name: Biomolecular nanotechnology
Year of enrolment: ☐ 1st Year ☐ 2nd Year ☐ **3rd Year and more**

The environmental monitoring of hormones represents a great public interest. Various studies have described the enormous effects of such molecules on humans and animals, even at very low concentrations [1]. Nevertheless, area-wide measurements are a major as the necessary measuring technology to detect such substances in concentrations of ng/l has only been available in laboratories. There is therefore an urgent need for easy-to-use measurement technology to detect potentially hazardous hormones in water.

The hypothesis of this work to develop a non-dispersive technique of a spectrometer with an electrically pumped single photon source as innovative system building block with enhanced performance for the measurement of lowest absorptions. The single photon source is based on QDs [2] as the actual photon source, for which the emission wavelengths are to be extended into the infrared range, and the DNA origami. DNA origami is used for place the single QDs on respective electrode structure, thereby isolating them for the formation of single photon sources. Both nanocomponents are combined into the QD-DNA origami. To achieve this, it is necessary to synthesize the QDs with emission wavelengths in visible (Vis), near infrared (NIR) and infrared (IR) spectrum region and optimize of QDs-DNA hybrids.

In this work, we synthesized water-based $AgInS_2$ (AIS), $Ag_2S$ core and AIS/ZnS core/shell QDs emitting in the Vis spectrum range, and organic PbS core and InAs/ZnSe core/shell QDs emitting in the NIR-IR range using the hot injection synthesis approach [3-5]. These QDs are characterized by high value of the photoluminescence (PL) quantum yield (up to 84%) and PL in the Vis-NIR-IR spectrum range from 470 to 1600 nm. The TEM and DLS analysis showed possibility to change the size of the nanoparticles by changing the synthesis conditions. Stabilization of the QDs with L-glutathione leads to increase the value of the PL decay times and stability of the QDs. The slower injection of the Ag and Na precursors during the synthesis leads to red shift of the PL maximum. Two different bioconjugation protocols for the QDs and the single-standard DNA (ssDNA) were successfully demonstrated. We also performed the first experiment of attachment of the QDs centrally within the free space of the DNA origami frame, aided by ssDNA extruded at specific locations on the DNA origami. By functionalizing QDs with complementary ssDNA strands, we conjugated the QDs to the DNA origami and created the first QD-DNA origami hybrid. This minimizes the influence of the DNA origami on the optical properties of the QDs and on charge transport. Our next steps are to optimize the transfer of organic quantum dots into water using water-soluble polymers.

**Keywords:** Quantum dots, DNA, hybrids, spectrophotometer, absorption.

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# 3D Printing of Responsive Biomaterials for Bacterial Infection Sensing

Ana María M. Mateo, Francesca Perin, Clara García-Astrain

*Student Name: Ana María Muñoz Mateo*
*PhD programme: Applied Chemistry and Polymers*
*Laboratory Group Name: FunPolySens POLYMAT*
*Year of enrolment:* ☐ *1st Year* ■ *2nd Year* ☐ *3rd Year and more*

Antimicrobial resistance (AMR) is a major global challenge, underscoring the urgent need for new antimicrobials, whose development relies on accurately replicating in vivo bacterial environments within in vitro experimental models[1]. In this context, 3D bioprinting has emerged as a promising strategy to recreate physiologically relevant tissue microenvironments and host–pathogen interactions. Additionally, integrating sensing elements into (bio)inks enables real-time, in situ monitoring of bacterial behaviour. Among various sensors, polydiacetylenes (PDAs) stand out due to their unique optoelectronic properties. These are synthesized through the polymerization of self-assembled PDA monomers, yielding blue, non-fluorescent liposomes that undergo a visible transition to red and fluorescent states in response to environmental changes or interactions with bacteria and biomolecules[2]. Here, we propose the development of (bio)inks with integrated sensing capabilities for real-time detection of bacteria and bacterial metabolites, which will be used to fabricate 3D (bio)printed infection models by stereolithography (SLA). To this end, PDA-based sensors are incorporated into hydrogel-based (bio)inks to enable colorimetric and fluorescent monitoring of multiple stimuli (Figure 1). 10,12-pentacosadiynoic acid (PCDA) was selected as sensor for its extensive use in sensing application and commercial viability, while the synthetic phospholipid 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC) was added to stabilize the liposomes. Gelatin methacryloyl (GelMA) was employed as hydrogel matrix due to its biocompatibility and printability. Preliminary results indicate the successful formulation of a printable PCDA/DMPC–GelMA ink, enabling the incorporation of the sensors into the GelMA matrix and exhibiting a pronounced blue-to-red colorimetric transition, alongside a fluorescence response, upon exposure to external stimuli.

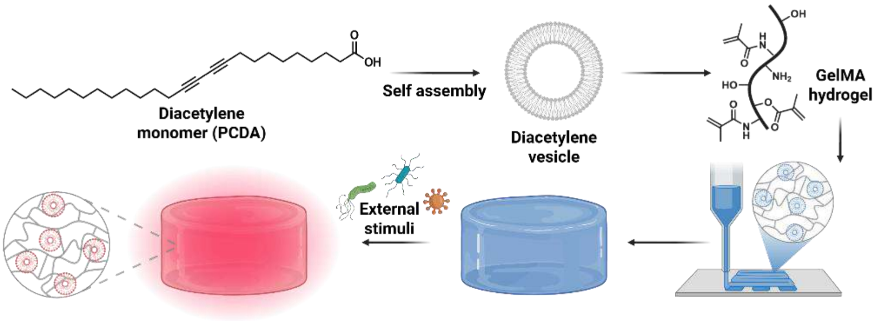

**Figure 1.** Schematic illustration of 3D printed hydrogel with incorporated liposomes.

**Keywords:** biosensing, 3D models, hydrogels, 3D printing, biomaterials.

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# Understanding and Improving Substrate Adhesion of Polymer Dispersions

Mohammadmahdi Negaresh, Maria Paulis, Shaghayegh Hamzehlou

*Student Name: Mohammadmahdi Negaresh*
*PhD programme: Applied chemistry and polymeric materials*
*Laboratory Group Name: Polymerization Processes Group*
*Year of enrolment:* ■ *1st Year* □ *2nd Year* □ *3rd Year and more*

Polymer dispersion adhesives, like pressure-sensitive adhesives (PSAs), involve three primary stages of adhesion: evaporation, deformation, and coalescence. The complex process of adhesion makes it difficult to understand the adhesion mechanism, which is highly material-dependent. The performance of an adhesive is usually tested by performing mechanical tests like tack, peel, and shear tests. However, the results of the tests tend to differ because of differences in sample preparation, operation, and company norms, which makes it difficult to compare and analyze the results. This problem can be overcome by using numerical simulations, which can help cut down on the cost and time of experiments. In our research, the possibility of simulating mechanical adhesive tests is offered by computational solid mechanics.

The tackiness of the adhesive is generally tested using a probe tack test, which assesses the short-time bonding ability of PSAs. In the process of probe contact and separation, the creation of cavities (air bubbles) may occur in the adhesive layer, which has a profound effect on the mechanical behavior. The PSA is assumed to be a hyperelastic-viscoelastic material. The non-linear elastic behavior of the material at large strains is modeled using a two-parameter Mooney-Rivlin model, and the viscoelasticity is modeled using a generalized Maxwell model formulated in a finite element environment. The Prony series is employed to model the multi-timescale stress relaxation and the overall time-dependent mechanical behavior of the adhesive. All simulations and model development are carried out in COMSOL Multiphysics using four adhesive formulations with distinctly different material properties.

**Keywords:** Pressure-sensitive adhesives, computational solid mechanics, Probe tack test, Hyperelastic–viscoelastic modeling, COMSOL Multiphysics

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# Cofactor loaded enzyme-polymer hybrids

Aitor Ontoria, Tatiana Guendulain, Ana Beloqui

*Student Name: Aitor Ontoria*
*PhD programme: Applied chemistry and polymeric materials*
*Laboratory Group Name: Polyzymes*
*Year of enrolment: ☐ 1st Year ☐ 2nd Year ■ 3rd Year and more*

Amine transaminases (ATAs) are enzymes with high potential in biotechnological applications. ATAs can be useful for the enantioselective production of compounds of high value such as chiral amines and enantiopure amino alcohols, which are considered as active pharmaceutical intermediates (APIs).[1] To carry the transamination reaction, ATAs require pyridoxal 5'-phosphate (PLP), which is eventually recovered after the reaction. There are several examples in literature where PLP is incorporated in reaction and storage media of these ATAs to avoid the leaching of the PLP from the active site of these proteins. Hence, this work proposes using polymers not only to confer enzyme stability but also to dress enzymes with rationally designed polymers capable of accommodating cofactors. The herein shown approach entails the covering of enzymes within a polymeric nanogel that host the required cofactor close to the enzyme, facilitating the diffusion of the cofactor to the active site of the enzyme and endowing a favorable microenvironment for the biocatalytic reaction.[3] Thanks to the polymeric layer, engineered enzyme nanogels exhibit tunable properties such as surface charge and relevant chemical motifs for cofactor immobilization. To test this, six different polymer compositions have been studied. Three of those — positively and negatively charged, and a zwitterionic polymer— have been assembled around the targeted ATAs (ω-Transaminase from *Halomonas elongata*, Transaminase $TR_2$ from *Acidihalobacter* and (R)-Selective transaminase from *Aspergillus fumigatus*).

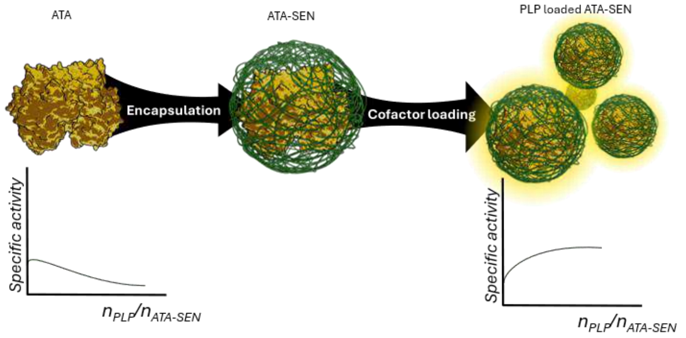

***Figure 1.*** Schematic representation of the protein-polymer conjugate (ATA-SEN), and the specific activities of the different catalysts.

**Keywords:** Transaminases, Encapsulation, Nanogels, Cofactor-confinement

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# Oragnocatalyzed polyacetal formation using catalytic acid:base complexes

Gabriela Pinheiro[1], Marta Ximenis[2], Gabriel Perli[3] Haritz Sardon[4]

*Student Name: Gabriela Pinheiro*
*PhD programme: Applied Chemistry and Polymeric Materials*
*Laboratory Group Name: Catalysis & Sustainable Polymers*
*Year of enrolment:* ■ *1st Year* ☐ *2nd Year* ☐ *3rd Year and more*

Polyacetals are synthesized by polycondensation, transacetalization, or ring-opening polymerization, but these approaches either require challenging cyclic precursors, or efficient removal or byproducts that induce material degradation resulting in limited molecular weight control[1], [2]. In this scenario polyaddition of diols to divinyl ether offers a more straightforward and atom-efficient route, however the permanent presence of the acid catalyst in the system can lead to polymer degradation[3]. In this work we aim to solve this limitation by employing acid:base complexes as catalysts to enable efficient polymer production while mitigating depolymerization. We identified the DBU:MSA complex as a latent catalyst through temperature-dependent reactivity studies with model compounds (Fig 1a). Acetal formation was only triggered above 70 °C, while no reaction occurred at lower temperature, revealing a clear on/off catalytic behavior (Fig 1b). In addition, the resulting acetals remained stable in the presence of water at room temperature, indicating suppressed acid activity under mild conditions (Fig 1c). These observations demonstrate that DBU:MSA operates as a thermally activated, latent catalytic system for acetal formation. Considering the thermal control over both the acetal formation and its hydrolysis the DBU:MSA complex stands as a promising catalyst for controlled polyacetal production.

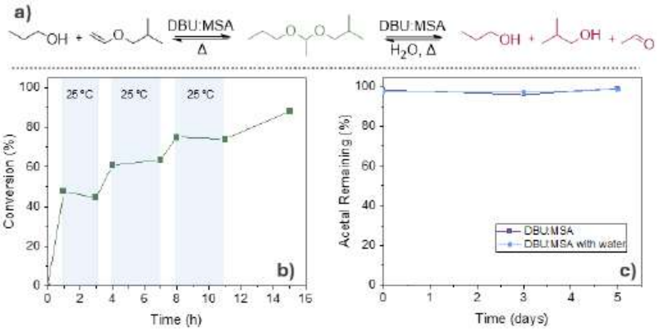

***Figure 1.*** *This is the caption for Figure 1*

**Keywords:** Polyacetal, Latent Catalyst, Polyaddition.

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# Pd-Catalyzed C($sp^2$)-N Directed Amidations of Tyrosine-Containing Peptides

Iván Pérez-Cubero[1], Arkaitz Correa[1]

[1]University of Basque Country (UPV/EHU), Department of Organic Chemistry I, Joxe Mari Korta R&D
Center, Avda Tolosa 72, 20018 Donostia-San Sabastian (Spain)

*ivan.perez@ehu.eus*

*Student Name: Iván Pérez Cubero*
*PhD programme: Química Sintética e Industrial*
*Laboratory Group Name: Catálisis sostenible: Métodos y computacional.*
*Year of enrolment:* ☐ *1st Year* ☐ *2nd Year* ■ *3rd Year and more*

Due to its importance in the pharmaceutical industry, multiple strategies have been developed for C–N bond formation. In this context, C–H activation has emerged as a powerful synthetic tool for the selective functionalization of nitrogen-containing substrates, including structurally complex and biologically relevant frameworks. In particular, our group has contributed to the development of late-stage metal-catalyzed functionalization methodologies applied to peptide-based systems[1]. Despite these advances, the incorporation of amides into aryl compounds remains a significant challenge, mainly due to their intrinsically low reactivity. While important progress has been achieved in structurally simple substrates[2], the present work proposes a practical and efficient methodology for the selective functionalization of carbamates in tyrosine-derived peptides.

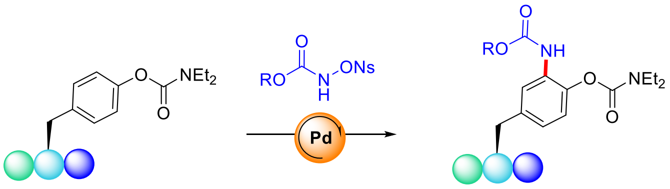

***Figure 1.*** *Directed C($sp^2$)-N amidations of Tyrosine-Containing Peptides*

**Keywords:** Amidation, Tyrosine, Palladium, Carbamate, C-H functionalization.

**Acknowledgments:** We are grateful to Ministerio de Ciencia e Innovación (PID2021-122889NB-I00, PID2024-158303NB-I00, PRE2022-104190, MCIN/AEI/10.13039/501100011033) for financial support.

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# Waterborne polymer dispersion crosslinked by the thiol-epoxy reaction

I.Rodriguez, J.Elgoyhen, R.Tomovska

*Student Name: Iker Rodriguez Mugica*
*PhD programme: Applied Chemistry and Polymers*
*Laboratory Group Name: Polymerization Processes Group (POLYMAT)*
*Year of enrolment:* ***x*** *1st Year* ☐ *2nd Year* ☐ *3rd Year and more*

Solvent-borne polymers have traditionally dominated the coating industry, but growing ecological concerns are driving a shift toward waterborne dispersions due to their lower VOC levels and reduced carbon footprints[1]. Despite these benefits, waterborne systems often exhibit inferior performance caused by the complexity of the film formation process[2]. This study addresses this limitation by investigating interparticle crosslinking through base-catalyzed thiol-epoxy[3] "click" chemistry—a robust, safer alternative to hazardous traditional crosslinkers like dihydrazides or polyfunctional amines. We developed a dual-latex strategy by blending methyl methacrylate/butyl acrylate/glycidyl methacrylate (MMA/BA/GMA) particles, functionalized with surface-accessible epoxy groups via seeded semibatch emulsion copolymerization, with a polythioether latex containing surface SH groups synthesized via sonopolymerization of diallyl terephthalate (DATP) and 2,2'-(ethylenedioxy)diethanethiol (EDDT). To counteract the mechanical softening typically associated with polythioether compounds, we leveraged the semicrystalline domains of the EDDT-DATP polymers to provide essential structural reinforcement. Upon the addition of a sodium hydroxide (NaOH) catalyst, the thiol-epoxy reaction facilitated efficient network formation. The resulting crosslinked films demonstrated significantly enhanced mechanical properties and substantially reduced water uptake compared to non-catalyzed reference blends. This research analyzes the critical interplay between chemical crosslinking and crystallization to identify the optimum balance for high-performance, sustainable coating applications.

**Keywords:** thiol-epoxy, click-chemistry, crosslinking, waterborne polymers

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FACULTY OF CHEMISTRY

# Synthesis and characterization of poly(4-vinylpyridine) functionalized membranes

U. Roldan, A. Gallastegui, D. Minudri, E. Gabirondo, N. Casado

*Student Name: Unax Roldan Rosas*
*PhD programme: Applied Chemistry and Polymeric Materials*
*Laboratory Group Name: Innovative Polymers Group (Polymat)*
*Year of enrolment: ☑ 1st Year ☐ 2nd Year ☐ 3rd Year and more*

Anion Exchange Membrane (AEM) based $CO_2$ electrolysis is an emerging technology for the electrochemical conversion of carbon dioxide into value-added chemicals and fuels, offering a promising route towards carbon-neutral energy systems. To fully exploit its potential, it is necessary to face the existing limitations by contributing to the development and innovation of advanced membrane materials, which is the main objective of this work.

This study focuses on the synthesis of functionalized membranes based on poly(4-vinylpyridine) (PVP) and their subsequent characterization. The AEM membranes are prepared via solvent casting method, starting with PVP, which undergoes a quaternization reaction and crosslinking. For this, the polymer is mixed with different dihalide reagents in a suitable solvent under controlled temperature and agitation conditions. Once a homogeneous reaction medium is obtained, the solution is cast into a Petri dish, where it undergoes a solvent evaporation process while the dihalide reacts with the polymer.

The prepared membranes are characterized to evaluate their physical, thermal, chemical and electrochemical properties. Physical properties are determined by evaluating the sorption capacity and volumetric expansion in both water and KOH. Chemical structure is analyzed by Fourier Transform Infrared Spectroscopy (FTIR), while thermal properties and stability are investigated using Differential Scanning Calorimetry (DSC). Ionic conductivity is measured both in-plane and through-plane to determine the performance of the membranes. In addition, ion exchange capacity and alkaline stability tests at different temperatures are conducted to assess their chemical robustness under operating conditions.

As a result, by establishing a correlation between the molecular composition and the mentioned properties, the most promising membrane can be identified. This will enable the future evaluation of its performance in an electrolytic cell, considering the required operating conditions and prioritizing sustainability and efficiency.

**Keywords:** synthesis, characterization, Anion Exchange Membranes (AEM), poly(4-vinylpyridine) (PVP)

# Novel Approaches to Flavin-Like Photochemistry on Earth-Abundant Metal Substrates

Alfredo Manuel Rotundo, Fernando Lopez Gallego, Luca Salassa

*Student Name: Alfredo Manuel Rotundo*
*PhD programme: Applied Chemistry and Polymeric Materials*
*Laboratory Group Name: Inorganic Photochemistry Lab*
*Year of enrolment:* ☐ *1st Year* ☐ *2nd Year* ☒ *3rd Year and more*

This work investigates the role of flavin-based photochemistry in promoting the dissolution of metal-bearing minerals under light irradiation. Owing to their versatile redox properties, flavins can act as efficient photosensitizers, generating reactive species capable of driving oxidative processes at mineral surfaces. Upon photoexcitation, flavins undergo redox cycling that facilitates electron transfer reactions, enabling the mobilization and solubilization of metal ions from solid substrates under mild conditions.

By exploiting these photochemical properties, this study explores how flavins can enhance mineral dissolution through light-driven redox pathways[1,2]. The findings highlight the potential of flavin-mediated photoreactions to control and accelerate mineral weathering processes, opening new perspectives for environmentally friendly approaches to metal extraction and geochemical transformations.

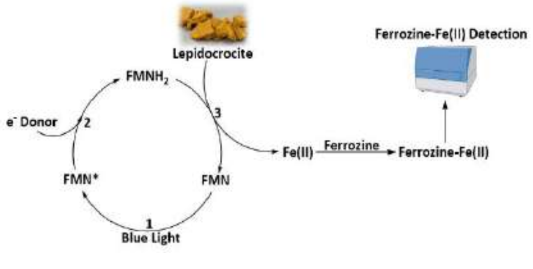

***Figure 1.*** *Proposed catalytic cycle for the reduction of Lepidocrocite to Fe(II) mediated by FMN and Ferrozine.*

**Keywords:** Flavin, Photocatalysis, Minerals, Dissolution, Lepidocrocite

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# Miniemulsion polymerization of cardanol methacrylate for high biobased content coatings

S. Rubio[1], A. Barquero[1], E. González[1]
[1]POLYMAT, Kimika Aplikatua saila, Kimika Fakultatea, University of the Basque Country UPV/EHU, Tolosa Hiribidea 72, 20018 Donostia – San Sebastián (Spain).
sara.rubio@ehu.eus

*Student Name: SARA RUBIO*
*PhD programme: Applied chemistry and polymeric materials*
*Laboratory Group Name: Polymerization Processes Group*
*Year of enrolment: ☐ 1st Year ☐ 2nd Year x 3rd Year and more*

Polymeric coatings play a crucial role in protecting different kind of materials, extending their service life, as well as enhancing their aesthetic appearance. With increasing sustainability concerns and regulations, the market of polymeric coatings has been focused on shifting from petroleum-derived raw materials to renewable alternatives. A wide range of renewable resources has been investigated for such application, including vegetable oils, lignin, tannins, cellulose and sugar alcohols. In this regard, agro-industrial residues and inedible biomass are viewed as more sustainable feedstock options, in which cardanol has attracted significant attention[1]. This is a non-edible agricultural byproduct of the cashew industry, valued for its abundance and affordability. Its molecular structure, featuring a phenolic group and an unsaturated alkyl chain, contributes to an effective combination of rigidity and flexibility, attractive for coating applications[2]. In this work, miniemulsion homopolymerization and copolymerization of cardanol methacrylate with other biobased monomers is investigated, targeting latexes with a minimum biobased content of 80 %. Additionally, taking advantage of the crosslinking potential of the unsaturated alkyl chain, different crosslinking strategies were evaluated to identify the most effective approach. These included variations in drying temperature, incorporation of drying agents, and the use of a photopolymerizable comonomer. The resulting latexes and polymer films were characterized in terms of water resistance and mechanical performance to assess their suitability for coating applications.

**Keywords:** biobased coatings, biobased polymers, miniemulsion polymerization, crosslinking

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# TAYLOR-MADE BLENDS OF POLYHYDROXYALKANOATES WITH IMPROVED MECHANICAL PROPERTIES AND PROCESSING BEHAVIOUR

Pilar Salsé, Belén Pascual, Itxaso Calafel

*Student Name: Pilar Salsé Rosera*
*PhD programme: Applied Chemistry and Polymeric Materials*
*Laboratory Group Name: Polymers and Composites' Rheology*
*Year of enrolment:* ☐ *1st Year* ☒ *2nd Year* ☐ *3rd Year and more*

Nowadays, the research and development of biomaterials is increasing due to the restrictions and the growing sustainability awareness of society. These materials exhibit some properties that make them similar to the fossil-based plastics, but they also present some drawbacks, such as high rigidity and a narrow processing window, that sometimes make their implementation challenging.

One of the most promising biopolymers is the polyhydroxyalkanoate (PHA) family. This kind of materials can be divided into two different types: the *short-chain length* ones (*scl-PHA,* which contain between three and five carbon atoms in their structure and present a rigid and brittle behaviour), and the *medium-chain length* ones (*mcl-PHA*, which have more than six carbon atoms in their structure and present a more ductile behaviour).

Considering the different characteristics exhibited by these two types of PHAs, the aim of this study is to develop new materials based on their blends that could present optimised mechanical properties and an adequate processing behaviour.

In order to determine their potential performance, several blends between *scl* and *mcl-PHAs* were prepared and characterised in terms of mechanical, thermal, rheological and morphological properties The miscibility of the blends was also evaluated to complete the study.

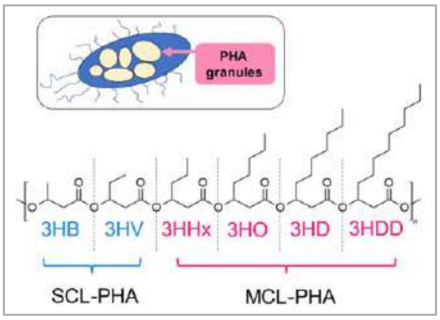

***Figure 1.*** *Differences in structure of PHAs (Bedade et al., 2021)*

**Keywords:** *Polyhydroxyalkanoates, blends, miscibility, rheological properties*

**References:**

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# Chaotic Printing as a Strategy for Enzyme Immobilization

Gorane Sansiñena, Manuel Eduardo Martinez, Ana Beloqui.

*Student Name: Gorane Sansiñena Emazabel*
*PhD programme: Applied Chemistry and Polymers*
*Laboratory Group Name: Polyzymes*
*Year of enrolment: ☒ 1st Year ☐ 2nd Year ☐ 3rd Year and more*

The spatial organization of enzymes is essential for optimizing cascade reactions in confined microenvironments. Precise enzyme positioning enables efficient transfer of reaction intermediates, minimizes diffusion losses, and enhances both catalytic efficiency and enzyme stability. Although several materials, such as polymers and metal–organic frameworks (MOFs), have been explored for enzyme immobilization and confinement, these approaches often provide limited control over enzyme distribution at the microscale.

In this study, we present a novel strategy to spatially organize enzymes using chaotic printing. This emerging fabrication technique enables the generation of highly ordered microstructures with predictable internal channels produced through chaotic advection. Using this approach, alginate microbeads containing glucose oxidase (GOx) and horseradish peroxidase (HRP) were fabricated. The chaotic flow generated during printing produced reproducible multilayered channels within the beads, enabling the spatial separation of GOx and HRP into defined compartments.

Following fabrication, the alginate beads were crosslinked with $CaCl_2$ to stabilize their internal architecture while maintaining permeability for substrate and intermediate diffusion. This configuration promotes efficient communication between enzymatic domains and facilitates intermediate transfer between GOx and HRP during cascade reactions. By employing this approach, enzymes are spatially organized into distinct micro- and nanoscale channels, allowing precise control over intermediate diffusion improving reaction efficiency. Increasing the numbers of channels increase the enzyme activity and the number of channels are tuneable, so enzyme activity is also tuneable.

Overall, this work demonstrates the potential of chaotic printing as a versatile platform for constructing multicatalytic systems with precisely defined microarchitectures, offering promising opportunities for applications in biosensing, biocatalysis, and synthetic biology.

**Keywords:** Enzyme immobilization, chaotic printing, cascade reaction, enzyme printing.

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# Investigation of the effect of Carbon Dots on the Crystallization Kinetics and Thermal Behavior of Poly(ε-caprolactone)

Fateme Shariatikia, Leire Sangroniz, Alejandro J. Müller

*Student Name: Fateme Shariatikia*
*PhD programme: Applied Chemistry and Polymeric Materials*
*Laboratory Group Name: Alejandro Müller's group*
*Year of enrolment:* ☐ *1st Year* ☐ *2nd Year* ☐ *3rd Year and more*

Carbon dots (CDs) are versatile nanomaterials[1] with sizes below 10 nm, displaying strong fluorescence and biocompatibility.[2] Their tunable surface chemistry makes them attractive as functional nanofillers in biodegradable polymers such as poly(ε-caprolactone) (PCL), where they can influence crystallization. In this work, the crystallization kinetics, morphology, and thermal behavior of PCL nanocomposites containing CDs were characterized and analyzed. Two sets of PCL/CDs were prepared by extrusion, employing non-functionalized and functionalized CDs. PCL nanocomposites with non-functionalized CDs showed poor dispersion, forming large aggregates (>1 μm) according to polarized light microscopy, which appear as dark regions within the polymer matrix. In contrast, the nanocomposites containing CDs functionalized with surface amine (–$NH_2$) groups exhibited highly homogeneous dispersions, with no observable aggregation even at high CD contents. Differential scanning calorimetry demonstrated that the incorporation of CDs increased the overall crystallization rate of PCL. This effect was significantly more pronounced in samples with homogeneous CD dispersion, highlighting the critical role of nanoparticle surface chemistry and dispersion quality. These results demonstrate that improved CD dispersion effectively enhances the crystallization rate of PCL and provide insight into the structure-property relationships of PCL-based nanocomposites.

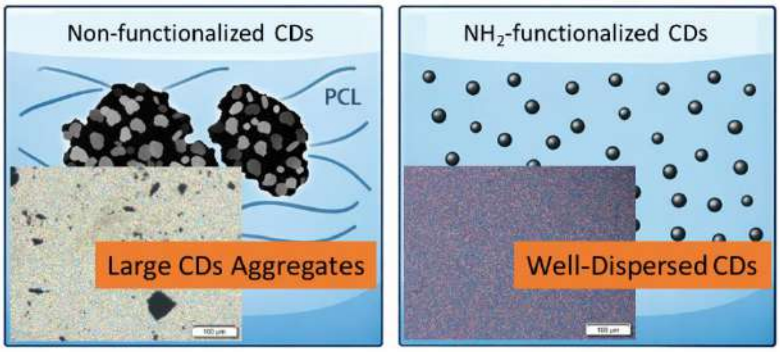

***Figure 1.** Difference between non-functionalized and functionalized CDs dispersion in PCL matrix.*

**Keywords:** poly(ε-caprolactone), carbon dots, crystallization kinetics, nanoparticle dispersion, thermal properties

**References**

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# Protective superhydrophobic coating for ceramic substrate

Yuanyuan Xin[1], Mato Knez[1.2], Aranzazu Sierra Fernandez[1]
[1] CIC nanoGUNE, Donostia/San Sebastian, Spain.
[2] Ikerbasque, Basque Foundation for Science, Bilbao, Spain

*Student Name:Yuanyuan Xin*
*PhD programme:* Physics of Nanostructures and Advanced Materials
*Laboratory Group Name: nano material group*
*Year of enrolment:* ☐ *1st Year* ☑ *2nd Year* ☐ *3rd Year and more*

The purpose of this research is to use advanced technique ALD to do the protective coating on the top of ancient ceramic, we reproduce ceramics which including HT (1000 ℃ fired), LT (700 ℃ fired) and RT (room temperature controlled) separately both of the red and white; then we used saturated sodium sulfur solution and did several immersion- drying corrosion cycles to simulate the degrading process of underground ceramics; finally we used TDMAS and ozone as precursors and applied the SiOx coating on the surface of substrate successfully. The results showed: 1. Firing temperature significantly influenced ceramic properties, particularly chemical composition and morphology. The white clays contain more kaolinite minerals [1], and the red clays contain more carbonite minerals. 2. The new phases generated obviously effect the color appearance of ceramics, the white ceramics got yellowish maybe relate to gypsum ($CaSO_4\cdot 2H_2O$), the red ceramics got darker might relate to the ferric sulfate ($Fe_2(SO_4)_3$). 3. The 30-cycle number of SiOx deposition showed more hydrophobicity compared with the 200-cycle number; the more roughness substrates LT showed superhydrophobic compared with the HT substrate at the same condition of 30 cycle number deposition.

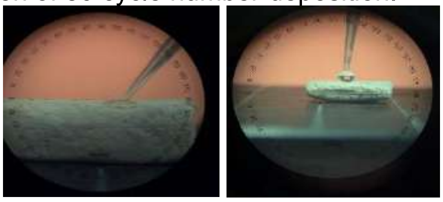

***Figure 1*** *water contact angle measurements of W-LT ceramic samples before and after $SiO_x$ deposition (30 cycles).*

**Keywords:** Atomic layer deposition, superhydrophobic, ceramics, deterioration,

**References**

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# Hydrophobicity gradients control function in short peptide self-assembled nanostructures

Irene Toledo Alday, Natalia S. Baranova, Ivan R. Sasselli

*Student Name: Irene Toledo Alday*
*PhD programme: Physics in nanostructures and advanced materials*
*Laboratory Group Name: Polymers and Soft Matter and Bottom-up Cell Biology and Bioengineering Lab*
*Year of enrolment: 2nd Year*

Supramolecular peptide assemblies (SPAs) are increasingly recognized as versatile building blocks for biomedical and nanotechnological applications due to their sequence-controlled self-assembly and tunable physicochemical properties.[1,2] However, establishing clear structure-property relationships that link peptide sequence to supramolecular organization remains challenging and requires an integrated experimental-computational approach. Here, we investigate a library of short peptides that self-assemble into fibrillar structures through sequence-encoded hydrophobicity gradients. Self-assembly onset is quantified by fluorescence spectroscopy through determination of critical aggregation concentrations (CACs), while AFM, circular dichroism, and FTIR spectroscopy confirm fibrillar morphologies and reveal sequence-dependent variations in secondary structure. These results show that subtle sequence modifications strongly influence intermolecular ordering, aggregate size, and critical concentration, with several systems displaying coexisting morphologies. To bridge experimental observables with molecular-level insight, we aim to identify experimentally accessible descriptors that correlate with coarse-grained molecular dynamics (CG-MD) simulations.[3] Importantly, we seek to determine whether these descriptors can also predict the performance of SPAs as antibacterial materials. This will be tested through experiments examining interactions between selected peptide assemblies and Pseudomonas aeruginosa bacterial strains, enabling evaluation of how supramolecular organization influences biological response. Overall, this integrative strategy connects macroscopic characterization, molecular modelling, and preliminary biological evaluation, providing a rational framework for the design of customizable SPAs with controlled architectures and tailored biological performance.[1,4]

**Keywords:** peptides, self-assembly, computational/experimental

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# IMPACT OF ALIPHATIC GLYCOL CHAIN LENGTH IN POLYCAPROLACTONE BASED RANDOM COPOLYESTERS

J. Torres-Rodríguez, M. Safari, R. A. Perez-Camargo, A. Mugica, M. Zubitur, A. Martinez de Ilarduya, H. Sardon and A. J. Müller

*Student Name: Juan Torres Rodríguez*
*PhD programme: Applied Chemistry and Polymeric Materials*
*Laboratory Group Name: Alejandro Müller group*
*Year of enrolment: ☐ 1st Year ☐ 2nd Year X 3rd Year and more*

The body of your abstract begins here. It should be an explicit summary of your presentation that states the problem, the methods used, and the major results and conclusions. It should be single-spaced in 10-point Arial font. Be sure to adhere to the word limitation **(250 words)** not including references and **not exceed 1 page**.

Poly(caprolactone) is a biodegradable polymer with the potential to reduce plastic pollution; however, its properties, such as high crystallinity, may require adjustment. Random copolymerization of copolymers with isodirmophic crystallization mode are a promising option to overcome these issues. [1]

In this study [2], we synthesized and characterized four series of biodegradable copolyesters: poly(ethylene succinate-*ran*-PCL) ($ES_xCL_y$), PBS-ran-PCL ($BS_xCL_y$), poly(octylene succinate-ran-PCL) ($OS_xCL_y$), and poly(dodecylene succinate-ran-PCL) ($DS_xCL_y$), through a two step synthetic protocol. The synthesized materials were extensively characterized using a range of techniques, including differential scanning calorimetry (DSC), hydrogen and carbon nuclear magnetic resonance (NMR), gel permeation chromatography (GPC), synchrotron wide and small-angle X-ray scattering (WAXS/SAXS), Fourier transform infrared spectroscopy (FT-IR), and polarized light optical microscopy (PLOM).

The systematic characterization conducted reveals that $BS_xCL_y$, $OS_xCL_y$ and $DS_xCL_y$ crystallize in an isodimorphic crystallization mode, while the $ES_xCL_y$ copolymers exhibit a novel comonomer exclusion/isodimorphism mode. Moreover, as the chain length increases, the pseudo-eutectic point shifts to a higher content of CL. Therefore, the composition and chain length significantly influence the thermal properties and crystallization behavior of these random copolyesters.

**Keywords:** Isodimorphic behavior, Exclusion/isodimorphic crystallization mode, Copolymerization, Pseudo-eutectic point, Poly(caprolactone)

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# Synchrotron X-ray radiation to study cellular reactivity of metal complexes

E.Zingales[1,2,3] C. Sanchez Cano,[1,2,4]
[1]Donostia International Physics Center, Spain
[2]Polimero eta Material Aurreratuak: Fisika, Kimika eta Teknologia, Kimika Fakultatea, Euskal Herriko Unibertsitatea UPV/EHU, Donostia, 20018, Spain
[3]CIC BiomaGUNE, Donostia, 20014, Spain
[4]Ikerbasque, Basque Foundation for Science, Bilbao, 48011, Spain

*Student Name:* Esteban Zingales
*PhD programme:* Química Aplicada y Materiales Polimericos
*Laboratory Group Name:* X-Ray Inorganic Biology
*Year of enrolment:* 4th Year

Metal complexes hold a nice promise as an intracellular catalyst for bioorthogonal reactions, as they enable precise non-metabolic transformations within the organism. Such catalysts have been used to activate selectively prodrugs, modify endogenous metabolites, or drive unnatural reactions inside cells, and are of great interest to develop innovative theranostics and targeted therapies. Therefore, understanding their intracellular targets, distribution and reactivity is of great importance for the future of the field of medicinal chemistry.[1,2]

Yet, traditional analytical methods used to study drugs inside cells cannot inform simultaneously on the localization and reactivity of metal complexes. For example, ICP-MS allow to study intracellular accumulation of metals, but destroys spatial information through homogenization. Mass spectrometry identifies fragments to distinguish intact catalysts from degradation products, but cannot provide this information with subcellular distribution. Finally, optical microscopy methods can provide chemical information with good resolution, but cannot be applied to many non-fluorescent metal complexes.

Synchrotron-based X-ray fluorescence (XRF) and X-ray absorption spectroscopy (XAS) are alternative methods to optical microscopy that can probe directly the metals on metal-based intracellular catalysts.[3] As such, XRF can provide label-free multielemental mapping with subcellular resolution, tracking intact and fragmented catalysts across organelles. Equally, XAS can reveal oxidation stated and coordination changes *in situ*, and with spatial resolution when combined into correlative approaches with XRF.

In this work, we present three projects where we applied synchrotron-based XRF and XAS to track metal complexes in biological systems, revealing their cellular fate and transformation mechanisms.

**Keywords:** synchrotron XRF; XAS/XANES, biological imaging, metal speciation, bioinorganic chemistry

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Thank You!

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