

35th Swiss Soft Days

Monday 17.03.2025 | 9h15-17h | Satigny

Program

9:15	Registration and coffee*	
9:55	Welcome	
10:05	Youwei Ma	Closed-Loop Recycling of Vinylogous Urethane Polymers and Their Composites
10:20	Dorina Opris	High-permittivity elastomers: Paving the way for next-generation applications
10:35	Gadi Slor	(De)polymerization from mixtures: towards natural recycling
10:50	Oya Tagit	Perfluorocarbon-loaded polymeric nanoparticles with tailored nanomechanical and surface properties for cell-specific uptake
11:05	Break-out sessions : Opportunities and choices in career development	
11:45	Boyang Zhou	Set number of plastic rearrangements at the onset to yielding
12:00	Yangxia Feng	Characterizing hydrogel behavior under compression with gel-freezing osmometry
12:15	Julien Bauland	Two-step aging dynamics in enzymatic milk gels
12:30	Lunch and poster session	
13:30	Madina Almukambetova	Double Symmetry Breaking in Filamentous Colloidal Tactoids
13:45	Savannah Gowen	Training and re-training disordered liquid crystal elastomer networks
14:00	Maryame Bina	Solid-supported textured polymer membranes as dual antifouling - antimicrobial functional surfaces



14:15	Anasua Mukhopadhyay	Fingerprinting Tau Oligomers with a 20 nm Diameter Nanopore from Pneumolysin
14:30	Yuechuan Lin	A New Method to Measure Pore Radius Distribution of Powders
14:45	Break and poster session	
15:15	Sara Catalini	Amyloid Aggregation in Mixed Whey Protein Systems: An Experimental Approach Across Multiple Length Scales
15:30	Simone Bertucci	Fabrication of Water-Based Photonic Paints Using Self-Assembled Block Copolymer Microparticles
15:45	Thomas Kainz	Colloidal Self-Assembly as Templating for 3D Second-Harmonic Photonic Crystals
16:00	Georges Formon	Expanding supramolecular polymers: from synthesis to responsiveness
16:15	Matteo Rutsch	Structure and dynamics of phytantriol-glycerol mesophases: Insights into the reverse micelle to lamellar phase transition
16:30	Closing remarks	

* Train RL5 from Geneva main station arrives at Zimeysa train station at 8:57 and 9:27.

It is about 5min walk to the dsm-firmenich site at Rue de la Bergère 7.

The guards at the entry gate will guide you towards the reception to receive a visitors pass and we'll guide you towards the meeting room.



ABSTRACTS

TALKS



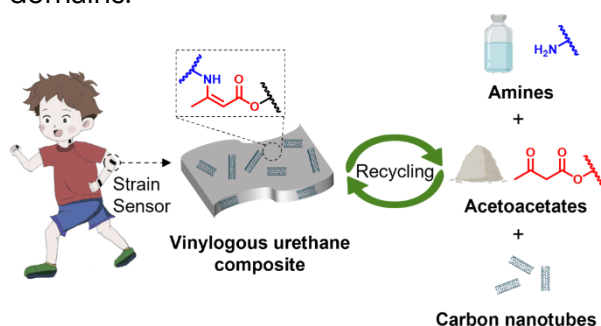
Closed-Loop Recycling of Vinylogous Urethane Polymers and Their Composites

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The development of mechanically robust and closed-loop recyclable polymers and composites represents an essential undertaking in the context of advancing a circular materials economy.¹ In this contribution, we show that vinylogous urethane (**VU**) polymer networks synthesized from bisacetoacetates with a skeleton of polyethylene glycol (**aPEG**) or polytetrahydrofuran (**aPTHF**), and tris(2-aminoethyl)amine (**TREN**), can be degraded by water or HCl, with the excellent recovery of bisacetoacetates (i.e., **aPEG** or **aPTHF**) and **TREN** components.^{2,3} Specifically, the hydrophilic **VU** networks with an **aPEG** skeleton undergo depolymerization in water, while the hydrophobic **VU** networks derived from **aPTHF** are depolymerized in a HCl/chloroform solvent mixture. The rate of depolymerization is controlled by temperature, the amount of water or HCl concentration, molecular weight of building blocks (i.e., **aPEG** and **aPTHF**), and composition of the starting materials. These last two parameters also allow one to tailor the mechanical properties of the final materials, which exhibit plastic-like or elastomer-like tensile behavior for **aPEG**- or **aPTHF**-derived networks, respectively. Moreover, incorporating fillers such as multi-walled carbon nanotubes (**MCNs**) and carbon fibers enhances the functionality of the resulting **VU** polymer composites without compromising their recyclability. This is corroborated by a case study, in which we demonstrate that the **aPTHF**-based **VU** composites containing 5 wt% **MCNs** can serve as a strain sensor, with the successful recovery of **aPTHF** and **MCNs** presented after its end of life.³ Overall, we anticipate that the **VU** chemistry explored here offers a versatile platform for synthesizing sustainable polymers and/or composites with closed-loop recyclability across diverse application domains.



References

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High-permittivity elastomers: Paving the way for next-generation applications

Prof Dorina Opris

Polymers with high and finely tunable dielectric permittivity are of great scientific interest due to their wide application potential, ranging from transducers and capacitors to Li-ion batteries. However, how much can the permittivity be increased, and how does this increase affect other properties? To answer these questions, we have modified the polysiloxanes with different types and amounts of polar groups and investigated how these chemical modifications affect different properties. We also explore the impact of filler addition on the properties of our polar silicones, focusing on enhancing the processability and functionality of thin films. The most promising polar silicone elastomers have also been investigated as dielectrics in actuators, sensors, energy harvesters, capacitive light-emitting devices, and electrolytes in solid-state Li-ion batteries and thus demonstrated their functionality.

(DE)POLYMERIZATION FROM MIXTURES: TOWARDS NATURAL RECYCLING

Gadi Slor

With approximately 400 million tons of plastic produced annually, the end-of-life (EoL) problem is one of the most pressing environmental issues today. Shockingly, only about 9% of this plastic is recycled, largely due to the challenge of managing mixed plastic waste streams that are difficult, if not impossible, to sort and process efficiently. In contrast, natural polymers like proteins, nucleic acids, and polysaccharides are produced on a billion-ton scale and are recycled in a perfectly sustainable way. These biopolymers undergo efficient and controlled synthesis and degradation within a highly complex matrix, in the presence of various monomers, organic molecules, salts, and more. If we could apply this synthesis and degradation scheme—paralleling a living cell to a reaction flask—we could significantly improve our recycling capabilities. Inspired by nature's remarkable ability to recycle its own polymers, in this talk I will present a closed-loop chemical recycling system capable of handling mixed plastic waste. The system is based on chemical recycling to monomer of polymers mixtures followed by selective polymerization of the yielded monomers mixture. This approach addresses one of the most critical challenges in plastic recycling: the efficient recycling of multi-material objects and films, and allows the recycling of complex mixed plastic waste streams.

PERFLUOROCARBON-LOADED POLYMERIC NANOPARTICLES WITH TAILORED NANOMECHANICAL AND SURFACE PROPERTIES FOR CELL-SPECIFIC UPTAKE

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Abstract

Poly(lactide-*co*-glycolide) nanoparticles (PLGA NPs) loaded with Perfluoro-15-crown-5-ether (PFCE) have been developed for *in vivo* ¹⁹F magnetic resonance imaging applications.¹ A slight modification of the formulation in terms of surfactant type led to different distribution profiles of PFCE phase through the polymer matrix with direct implications on the nanoparticle internal structure. While the non-ionic surfactant polyvinyl alcohol (PVA) facilitated the formation of multi-core particles with PFCE phase distributed as multiple small domains through the nanoparticle (multi-core particles, MCPs), the anionic surfactant sodium cholate (NaCh) packed the PFCE phase as a single domain within the core of the nanoparticles (core-shell particles, CSPs). This difference in the nanoparticle ultrastructure further impacted the hydration profile of the MCPs and CSPs, giving rise to significantly different nanomechanical properties (52 MPa and 120 MPa, respectively) as demonstrated by atomic force microscopy.² The impact of the surfactant on the NP surface chemistry was evidenced by their protein corona, which was significantly greater in CSPs. *In vitro* studies showed a higher uptake of MCPs by RAW macrophages but a preference for CSPs by HeLa cells. (Fig. 1). Overall, our study establishes a direct link between the type of surfactant used in nanoparticle formulation and the resulting internal structure, stiffness, and protein corona, all of which significantly influence particle-cell interactions. Our findings underscore the potential of tailoring particle stiffness and architecture to achieve cell-specific delivery in therapeutic and theranostic applications, where uptake efficiency by the biological targets is paramount.

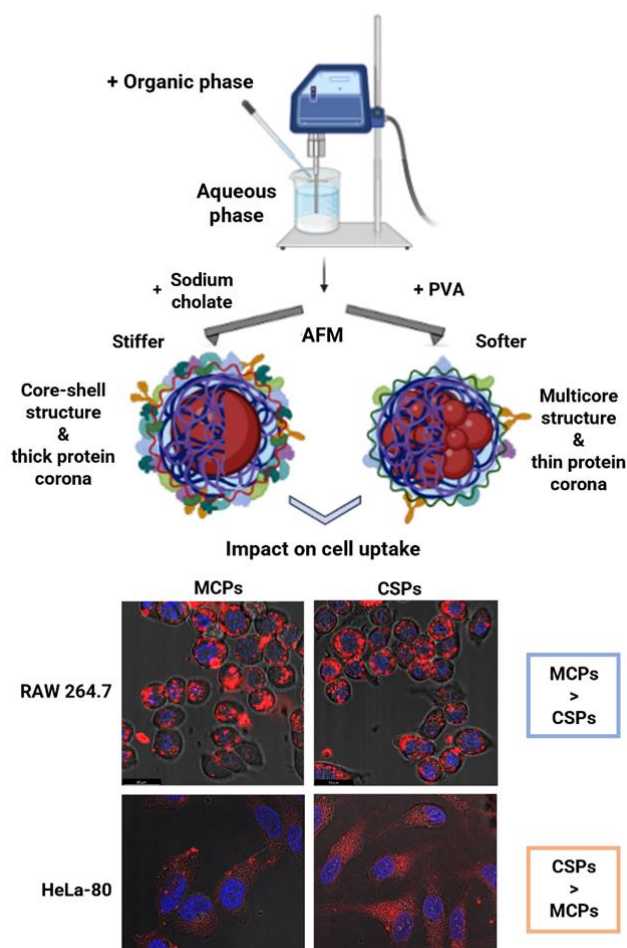


Figure 1. Surfactant-driven tailoring of the internal structure, stiffness, and protein corona of PFCE-loaded PLGA nanoparticles for cell-specific uptake.

¹ Staal, et al. In vivo clearance of ¹⁹F MRI imaging nanocarriers is strongly influenced by nanoparticle ultrastructure. *Biomaterials* 2020, 261, 120307.

² Vicente, et al. Perfluorocarbon-loaded poly(lactide-*co*-glycolide) nanoparticles from core to crust: multifaceted impact of surfactant on particle ultrastructure, stiffness, and cell uptake. *ACS Applied Polymer Materials* 2025,

<https://doi.org/10.1021/acspm.4c03360>

Published March 3, 2025



Set number of plastic rearrangements at the onset to yielding

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Soft jammed materials subjected to a constant strain rate exhibit a stress relaxation process upon shear cessation that eventually leads to a finite residual stress. Investigations revealed that when shear is stopped within the steady-state regime, where the stress has reached a constant value, the residual stresses systematically decrease with increasing shear rate (1-4).

We here explore the response to shear cessation when the application of a shear rate is stopped within the transient regime to steady state. Our experiments reveal that the residual stress depends on strain and is independent of the shear rate when the experiment is stopped at 'moderate' strains. This strain dependence of the residual stress contrasts with the strain-rate dependence of the stress observed during the application of the shear rate.

This suggests that strain encodes a fixed number of plastic rearrangements, which occur regardless of how fast this strain is reached. When the system is deformed too quickly, plastic rearrangements do not have time to occur within the experimental time scale, such that the system is elastically overloaded. Consistent with this interpretation, we find that the stresses obtained during the application of the strain rate matches the residual stress once the shear rate is sufficiently slow. Residual stresses thus effectively reflect the stresses observed under quasi-static loading conditions.

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Characterizing hydrogel behavior under compression with gel-freezing osmometry

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Abstract

Hydrogels are particularly versatile materials that are widely found in both Nature and industry. One key reason for this versatility is their high-water content, which lets them dramatically change their volume and many of their mechanical properties -- often by orders of magnitude -- as they swell and dry out. Currently, we lack techniques that can precisely characterize how these properties change with water content. To overcome this challenge, here we develop Gel-Freezing Osmometry (GelFrO): an extension of freezing-point osmometry. We show how GelFrO can measure a hydrogel's mechanical response to compression and shrinkage in response to an applied osmotic pressure, while only using small, 100 μ L samples. Because the technique allows measurement of properties over an unusually wide range of water contents, it allows us to accurately test theoretical predictions. We find simple, power-law behavior for both mechanical and osmotic responses, while these are not well-captured by classical Flory-Huggins theory. We interpret this power-law behavior as a hallmark of a microscopic fractal structure of the gel's polymer network and propose a simple way to connect the gel's fractal dimension to its mechanical and osmotic properties. This connection is supported by observations of hydrogel microstructures using small-angle x-ray scattering. Finally, our results motivate simplifications to common models for hydrogel mechanics, and we propose an updated hydrogel constitutive model.

References

Yanxia Feng, Dominic Gerber, Stefanie Heyden, Martin Kröger, Eric R. Dufresne, Lucio Isa, and Robert W. Style, *arXiv:2407.13718*.



Two-step aging dynamics in enzymatic milk gels

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Abstract : Colloidal gels undergo a phenomenon known as physical aging, i.e., a continuous change of their physical properties with time. To date, most of the research effort on aging in gels has been focused on suspensions of hard colloidal particles. In this work, we tackle the case of soft colloidal “micelles” comprised of milk proteins, in which gelation is induced by the addition of an enzyme. Using time-resolved mechanical spectroscopy, we monitor the viscoelastic properties of a suspension of colloidal micelles through the sol-gel transition and subsequent aging. We show that the microscopic scenario underpinning the macroscopic aging dynamics comprises two sequential steps. First, the gel microstructure undergoes rapid coarsening, as observed by optical microscopy, followed by arrest. Second, aging occurs solely through a contact-driven mechanism, as evidenced by the square-root dependence of the yield stress with the elastic modulus measured at different ages of the gel. These results provide a comprehensive understanding of aging in enzymatic milk gels, crucial for a broad range of dairy products, and for soft colloids in general.

Double Symmetry Breaking in Filamentous Colloidal Tactoids

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Understanding dynamics of liquid crystalline tactoids under external forces is of great importance due to their potential applications in optics, medical devices and displays. However, only recently have tactoids started to be studied systematically under external forces, in particular, by extensional flow [1]. Here, we subject tactoids to a shear flow field and study their deformation dynamics upon varying conditions of shear and time scales. Using amyloids and nanocellulose to form tactoids from model filamentous colloids with opposite sequence of chirality amplification (left-handed mesoscopic→right-handed cholesteric for amyloids [2]; right-handed mesoscopic→left-handed cholesteric for nanocellulose [3]), we show a complex deformation mechanism in their shape and internal structure under shear flow. When tactoids deform perpendicularly to their long axis, a double symmetry breaking occurs in both their contour shape, with the emergence of a kink, and their orientation of nematic field. We further show that the mesoscopic chirality of the building blocks directs the position of the kink, with the macroscopic tactoid asymmetry being mirrored when inverting the mesoscopic chirality of the constitutive filamentous colloids, e.g. from the left-handed amyloids to the right-handed nanocellulose.

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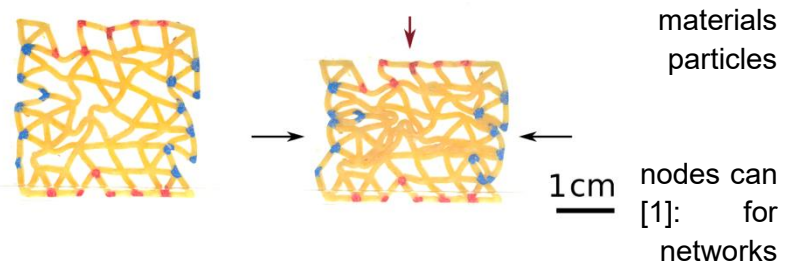


Training and re-training disordered liquid crystal elastomer networks

Savannah Gowen

Disordered elastic networks are model for disordered systems from jammed to polymers. It has been shown that metamaterials formed from macroscopic disordered network arrays of bonds and be trained to exhibit novel elastic functions example, unlike most natural materials these

can be trained to display a negative Poisson's ratio in which they respond to compression along one axis by contracting along all the others[2]. Another novel elastic property is inspired by protein allostery: the binding of a molecule at one site in a protein triggers the ability of a distant site to bind to another molecule. Likewise, this action-at-a-distance can be implemented mechanically: Applying strain locally to a set of source nodes in the material triggers a strain response at a distant set of target nodes [3-5]. This work investigates both the ability to train for function and then to erase that function on-demand in macroscopic metamaterials made from liquid crystal elastomers (LCEs) [6]. We first show how macroscopic liquid crystal elastomer networks can be tuned via directed aging to induce an auxetic response. We then show that the arrays can be reset and re-trained for another local mechanical function, allostery, thus demonstrating pluripotent functionality.



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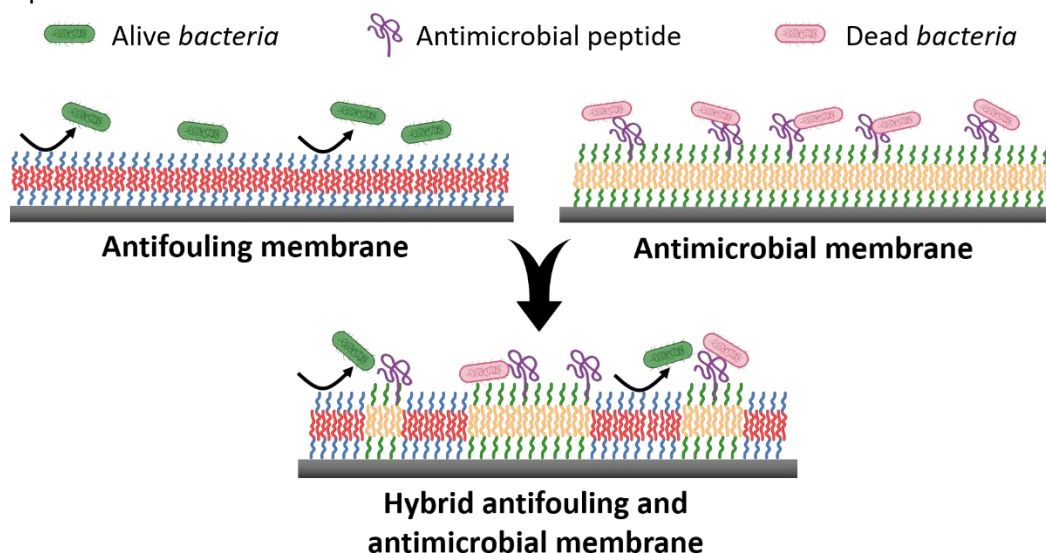
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Solid-supported textured polymer membranes as dual antifouling – antimicrobial functional surfaces

Maryame Bina, John P. Coats, Michal Skowicki, Mirela Malekovic, Voichita Mihali, Cornelia G. Palivan
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Nanotextured surfaces are widely found in nature and exhibit a variety of properties, such as superhydrophobicity, bacteria repellence, exceptional adhesion or structural colours. Traditional methods for manufacturing these surfaces, including physical or chemical patterning, are costly and require specialised equipment. Here, we introduce a biomimetic approach utilising the amphiphilic property of two dissimilar diblock copolymers as the driving force for their self-assembly, similar to how amphiphilic lipids form biological membranes. However, contrary to naturally occurring lipids, polymers offer enhanced mechanical stability and chemical versatility, thus allowing for the fine tuning of their properties. The membranes are composed of PEO-*b*-PEHOx and PMOXA-*b*-PDMS as the two amphiphilic diblock copolymers mixed at various concentrations. PEO exhibits antifouling properties, while PMOXA features a functional azide end group suitable for bioconjugation. These fully synthetic, solid-supported planar membranes, undergo phase separation, forming domains embedded within a continuous phase. The dissimilar properties of each block and the molar ratio of the copolymers in the mixture were the key parameters to induce nanoscale phase separation of the planar membranes.¹ Subsequently, by conjugating an antimicrobial peptide, KYE28, onto the phase separated polymer membrane, we create a multifunctional coating that significantly reduces bacterial attachment and growth. The combination of the antifouling PEO and the antimicrobial KYE28 produces a synergistic effect, resulting in a substantial decrease in bacterial proliferation.² Although this study presents only one example of application of phase separating polymer membranes, such hybrid polymer surfaces offer endless possibilities for the conjugation of biomolecules (enzymes, proteins, DNA strands, or antibodies) or nano assemblies, including nanoparticles or micelles.



References

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Fingerprinting Tau Oligomers with a 20 nm Diameter Nanopore from Pneumolysin

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Biological nanopores are emerging as powerful sensing tools for single-molecule analysis of nucleic acids, peptides, and proteins.¹ However, the limited size of existing biological nanopores presents a long-standing challenge for transporting large-size, full-length proteins in their natively folded state. Here, we introduce a stable, low-noise, cylindrical transmembrane pore formed by self-assembly of Pneumolysin (PLY) toxin.² *In situ*, assembly of the PLY nanopore occurred in a single step directly on a lipid bilayer upon application of a potential difference of 100 mV. Electrical resistance measurements revealed a diameter of approximately 20 ± 2 ($N = 50$) nm of membrane-inserted PLY nanopores. This exceptionally large nanopore enabled accurate single-molecule resistive-pulse sensing for the estimation of the volume and shape of folded proteins, ranging in size from FAB (≈ 50 kDa) to tetramers of concanavalin A (4×28 kDa = 112 kDa). We used PLY pores to detect differences in the volume of single proteins within a mixture and estimated the size distribution of tau protein (monomer ≈ 45 kDa) and its oligomers from dimers to hexamers in solution. By combining volume analysis with single-particle shape approximation, we uncovered details of Tau oligomerization at nanomolar concentrations. The novel PLY nanopore shows strong promise for advancing the quantification and characterization of heterogeneous amyloid oligomers as biomarkers.

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A New Method to Measure Pore Radius Distribution of Powders

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Author: Yuechuan Lin, Adam Burbidge, Josep Busom Descarrega, Ilaria Gaiani, Sidhanth Tyagi

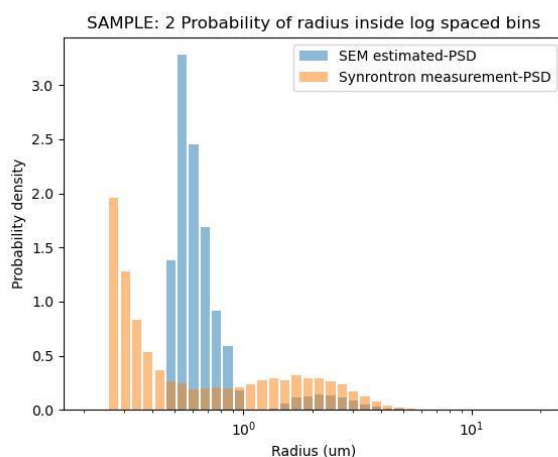
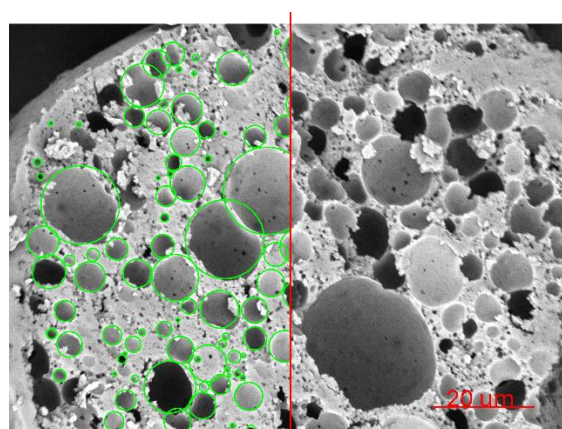
Abstract:

Pore radius distribution is one of the main metrics to characterize the internal porous structure of food [1,2]. State of the art techniques involve 3D tomography and 3D segmentation by thresholding [3,4]. However, resolution of x-ray tomography is limiting the minimal detectable pores. Voxel size of State-of-the-Art synchrotron X-ray tomography is on the order of 0.1 micron, meanwhile the smallest pores radius in the samples we want to study are around 0.5 micron. The resolution is not enough to resolve the smallest pores based on our experience.

To close the gap on resolution, we developed a new technique based on automated Scanning Electron Microscope (SEM), object detection model, and mathematical transformation to measure the pore size distribution of porous powder.

We first prepare the sample by cutting the powders to expose the internal structure. We then developed a two-stage scanning routine combining SEM and custom-trained object detection model to detect exposed pores for each sample. We name the radius of exposed pores as chord radius to distinguish from the spherical pore radius. Finally, we developed a mathematical transformation to convert the chord radius distribution into pore radius distribution.

To validate our method, we measured the pore radius distribution of 5 food powder sample with our method and synchrotron x-ray tomography. We reached the conclusion that our method has better resolving power for smaller pores ($\sim 0.5\mu\text{m}$) at the same time agree with the synchrotron measurement for larger pores ($\sim 2\mu\text{m}$). Our method is also more cost effective than the synchrotron method.



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Amyloid Aggregation in Mixed Whey Protein Systems: An Experimental Approach Across Multiple Length Scales

Sara Catalini

The fundamental principles underlying the complexity of protein assembly, particularly in mixed protein systems and crowded environments [1], remain poorly understood. Despite significant progress in the field, the molecular mechanisms driving protein aggregation and gelation in these environments continue to present challenges. This study provides crucial molecular, structural, and viscoelastic [2] insights into the aggregation and gelation processes of pure and mixed aqueous solutions of β -lactoglobulin and albumin whey proteins [3]. Using a multi-technique approach that spans length scales from the molecular to the macroscopic [4], we present a more comprehensive understanding of protein aggregation in complex systems. Our results demonstrate that under low pH and heat denaturation, β -lactoglobulin tends to form highly ordered amyloid-like aggregates [3, 5], while bovine serum albumin forms distinct non-amyloid aggregates [3]. In the presence of crowding agents, all protein solutions tested undergo a transition to composite gel networks with molecular origins that vary depending on protein composition [3]. Notably, the study emphasizes the ability to control the amyloid aggregate content, which has a significant impact on the structural, rheological, and viscoelastic properties of these composite gels. Such control over gel structure and viscosity is critical for applications in the food industry, as these properties are key to determining the softness, texture, and overall quality of food products, offering valuable insights for the design of texture-modified foods and other protein-based systems.

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Fabrication of Water-Based Photonic Paints Using Self-Assembled Block Copolymer Microparticles

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Since ancient times, colors and paints have played a fundamental role in human culture and technology. In modern days, paints primarily use synthetic pigments or dyes embedded in a polymeric binder, allowing for greater vibrancy and color control. These pigments, both organic and inorganic, owe their coloration to selective absorption of certain light wavelengths. Although versatile, commonly used pigments present dull tints and tend to fade over time. As an alternative to conventional techniques, recent research has concentrated on replicating the structural coloration found in nature. Structural color emerges from the interaction of light with a nanostructured material. In photonic crystals, light interacts with a structure consisting of a periodic nanoscale alternation of two materials with distinct refractive indices. This produces a spectral region of high reflectivity, known as Photonic Band Gap (PBG). Within this framework, we fabricated water-dispersed photonic pigments by leveraging the three-dimensional confined self-assembly of block copolymers (BCPs) within emulsion droplets. The resulting microspheres, composed of poly(2-vinylpyridine)-*b*-poly(methyl methacrylate) (P2VP-PMMA), exhibit structural coloration arising from their internal lamellar organization. To enhance their optical response, we introduced 2,4,6-triodophenol, a high-refractive-index molecule that selectively binds with one of the polymer blocks. By precisely controlling the amount of this molecular additive, we achieved tunable coloration across the visible spectrum with enhanced color brilliance due to the increased dielectric contrast. Subsequently, we formulate a photonic paint by mixing a water-soluble polymer binder with the microparticles to enhance the system stability, while simultaneously improving the overall color vividness. This system was thoroughly characterized, with a focus on performance criteria governed by the balance between the components within the formulation.

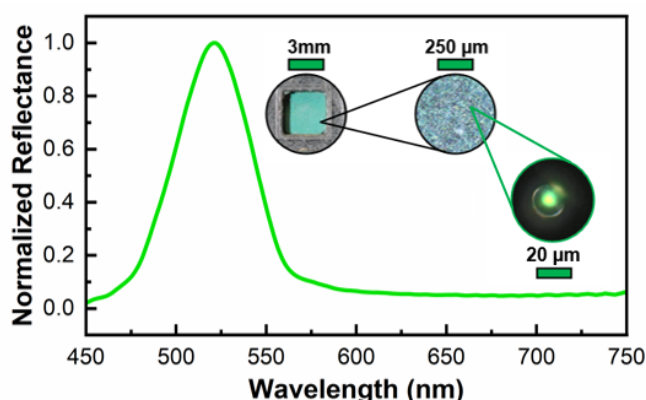


Table of Content. From macro to micro: digital photographs and microscope images of our paints at increasing magnification and relative reflectance spectrum



Colloidal Self-Assembly as Templating for 3D Second-Harmonic Photonic Crystals

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Three-dimensional nonlinear (second-harmonic) photonic crystals can simultaneously generate different non-linear processes, such as second-harmonic generation (SHG), optical parametric amplification, and other sum- and difference-frequency processes [1, 2]. However, creating large crystals in all three dimensions, mainly in the z direction, presents a considerable challenge, primarily due to the chemical inertness of metal oxides [3 – 5].

This study shows the first demonstration of colloidal-crystal-templating for a second-order optical material. We selectively synthesized monodisperse nanospheres with tunable unit sizes to self-assemble polystyrene opals with different band gaps (Fig. 1 a, b, e). These serve as templates for infiltration with barium titanate sol-gel. After a calcination step, we obtained an inverse fcc network of tetragonal barium titanate (Fig. 1 c). We fabricated samples with unprecedented sizes for single domains: > 3000 unit cells in x, y directions and > 100 in z (Fig. 1 d, f). The achieved optical reflectivity values are above 80% throughout the fabrication. We can engineer the final photonic band gap over the entire optical range, matching it both to material and setup requirements (Fig. 1 g).

We successfully replicated the photonic network into a second-order material. For the first time, we demonstrated a linear photonic band gap from a fully scalable three-dimensional photonic crystal made of a $\chi^{(2)}$ optical material. Our approach overcame previous limitations, especially stacking in the z -direction, while maintaining full tunability of the initial unit cell [3]. Reverse engineering of the final band gap wavelength to both avoid the materials absorption regime and match the available laser setups enables the experimental investigation of SHG generated within a band gap, such as inhibited spontaneous emission [6].

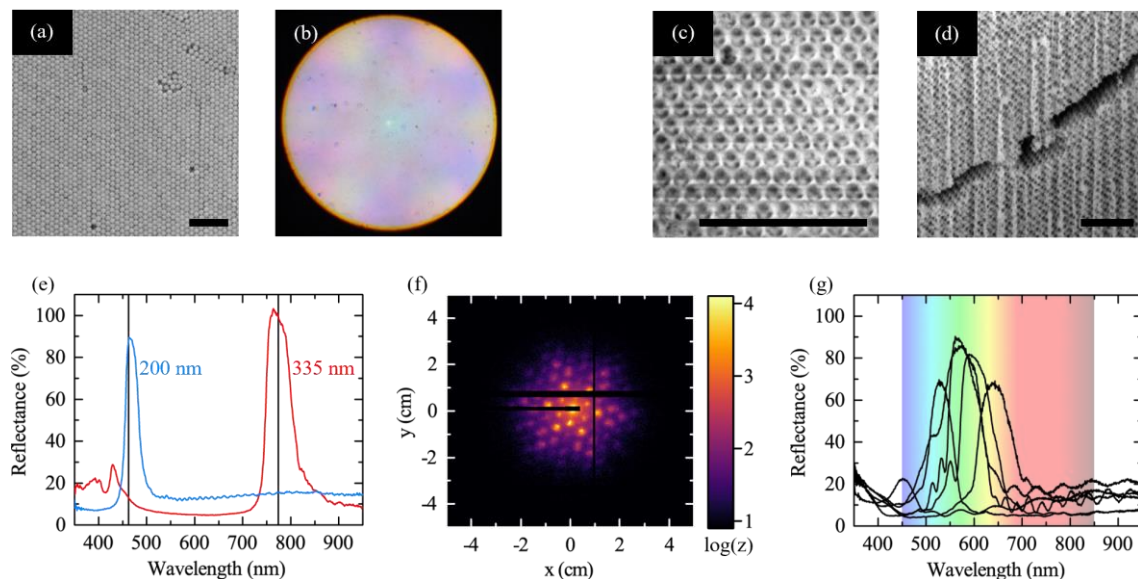


Fig. 1 Polystyrene face-centered cubic opal: (a) Scanning electron microscopy in (111) direction, (b) Optical microscope k -space image, (e) Reflectance spectra with calculated bandgap positions (vertical lines) for different initial PS bead sizes; Barium titanate inverse fcc crystal: (c) SEM in (111) direction, (d) Focused ion beam-SEM cross-section, (f) Ultra-small angle X-ray spectroscopy 2D diffraction pattern; (g) Reflectance spectra for different inclinations with optical range color coding; All scale bars are 2 μm .

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EXPANDING SUPRAMOLECULAR POLYMERS: FROM SYNTHESIS TO RESPONSIVENESS

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Supramolecular polymers (SMPs) have garnered significant interest due to their inherent stimuli-responsiveness,¹ which imparts advanced properties such as self-healing, reprocessability, and shape memory.² However, synthesizing these materials typically requires de novo synthesis, limiting their mechanical properties. Additionally, endowing them with responsiveness to new stimuli (e.g., light) often necessitates a complete redesign of the supramolecular motifs, involving laborious synthetic efforts.³ Recent developments in our lab aim to streamline the synthesis of responsive materials by either modifying commercial polymers or adopting an additive-based systems approach.

Creating supramolecular materials from commercially available polymers is a promising strategy to implement responsiveness into widely used materials, thereby increasing applicability and expanding their range of properties (Figure 1a). In our first approach, we depolymerized glycol-modified polyethylene terephthalate (PETG) and end-capped it with the 2,6-bis(1'-methylbenzimidazolyl)pyridine (Mebip)⁴ tridentate ligand, in one or two steps. Metallosupramolecular polymerization yielded glassy polymers that displayed comparable stiffness to the parent polymer and excellent optical and thermal healability. Similarly, we created supramolecular networks by grafting azide-modified 6-(1'-methylbenzimidazolyl)pyridine (MBP)⁵ bidentate ligand onto polybutadiene in a single step. The addition of metal ions (Zn^{2+} , Ni^{2+} , and Mg^{2+}) yielded metallosupramolecular rubbers whose properties could be tuned by varying the metal center and the metal-to-ligand ratio.

Alternatively, by adopting a systems approach,⁶ we developed isothermally light-responsive supramolecular gels and networks (Figure 1b). These networks, which are supramolecularly crosslinked either by the self-dimerizing hydrogen-bonding ureidopyrimidinone (UPy) or metal-ligand complexes with Mebip, are typically irresponsive to low-power light. By blending a photoacid generator into the system, light irradiation induces the release of hydrochloric acid, which protonates the supramolecular moieties, disrupting the supramolecular crosslinks. These isothermal transformations enable solid-to-liquid transitions by de-crosslinking these networks. This approach was applied to achieve isothermal de-bonding on demand in a rapid and efficient manner. With these novel approaches to creating supramolecular polymers and systems, we aim to simplify and expand the applicability of this class of materials by enhancing their modularity and broadening the range of their properties.

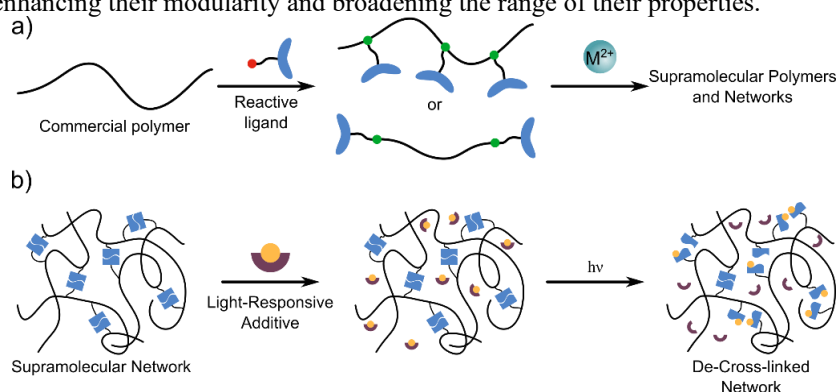


Figure 1: Schematic representation of a) synthesis of supramolecular polymers from commercial polymers, b) systems approach to achieve light-responsive networks.

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Structure and dynamics of phytantriol–glycerol mesophases: Insights into the reverse micelle to lamellar phase transition

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Lipidic mesophases (LMPs) are lyotropic liquid crystals formed by the self-assembly of amphiphilic compounds in solvents [1]. LMPs typically use water as a solvent, offering a rich variety of phase symmetries with distinct physicochemical properties, making them valuable for both fundamental and applied research [2]. However, studies on LMPs in non-aqueous solvents are scarce [3,4] and the fundamental understanding of how the dynamics relate to the composition and structure remains limited [5,6]. In this study, we replaced water with glycerol as the solvent to form LMPs with phytantriol, a commonly used, uncharged amphiphile. Combined small-angle x-ray scattering (SAXS) and differential scanning calorimetry (DSC) reveal a weakly exothermic reverse micelle (L_2) to lamellar (L_α) phase transition, which occurs at higher temperature as the glycerol content is increased. Using Broadband dielectric spectroscopy (BDS), we observed how the dynamics of phytantriol are governed by the composition and symmetry of the LMP: Increasing glycerol content decreases the relaxation time of the Debye- and α -relaxation, therefore exerting a plasticizing effect. The change in long-range order of phytantriol during the $L_2 - L_\alpha$ phase transition reveals a decrease in the conductivity relaxation time. The introduction of a net orientation of phytantriol further reveals a new relaxation process—the dipole–matrix interaction—exclusive to the L_α phase. These results highlight the value of combining BDS with structural and thermal analyses for a deeper understanding of the dynamics in soft matter systems. In addition, our developed system provides a straightforward platform to host non-aqueous reactions under soft nanoconfinement and opens new avenues for the study of biomolecular solvation.

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