# Topical Session
# Artificial Cell

Wednesday 02 June 10:40 – 12:30

# Active cell deformation through actin assembly, a biomimetic approach

**Cécile Sykes**

*Team "Active Cell Matter"*, Département de Physique, Ecole Normale Supérieure, LPENS UMR 8023
24 rue Lhomond, 75005 Paris, France

*Corresponding author:* cecile.sykes@phys.ens.fr

The mechanism of cell functions such as motility and division are approached using soft matter physics. We conceive stripped-down experimental systems that reproduce cellular behaviours in simplified conditions: cytoskeleton dynamics are reproduced on liposome membranes[i],[ii] (Figure 1). Complementary to the encapsulation approach[iii] , the "outside geometry" allows for soft matter variables to be tuned, such as membrane tension and the structural details of the cytoskeleton architecture. We obtain a phase diagram for conditions of inward or outward membrane deformations generated by actin dynamics[iv]. We also observe buckling and wrinkling under osmotic deflation[v], thereby confirming that actin networks are elastic and follow the generic mechanism of buckling and wrinkling found in various systems spanning from pollen grains to the development of the gut or the brain.

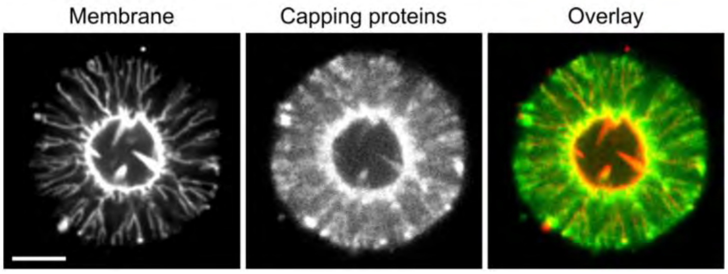


Figure 1: The dynamic actin cytoskeleton (marked by the presence of capping proteins, *Alexa Fluor 488 $C_5$-maleimide, green*) is able to deform the membrane (*TexasRed-DHPE, red*) inward (spikes towards the liposome center) and outward (tubes emanating from the liposome membrane). Scale bar: 5µm.

## References

---

[i] C. Simon, V. Caorsi, C. Campillo, **C. Sykes**, "Interplay between membrane tension and the actin cytoskeleton determines shape changes", *Physical Biology*, 5(6):065004, doi: 10.1088/1478-3975/aad1ab. (2018)

[ii] A. Allard, M. Bouzid, T. Betz, C. Simon, M. Abou-Ghali, J. Lemière, F. Valentino, J. Manzi, F. Brochard-Wyart, K. Guevorkian, J. Plastino, M. Lenz, C. Campillo*, **C. Sykes***, "Actin modulates shape and mechanics of tubular membranes" *Science advances, **6** : eaaz3050* (2020)

[iii] L.-L. Pontani, J. van der Gucht, G. Salbreux, J. Heuvingh, J.-F. Joanny, **C. Sykes**, "Reconstitution of an actin cortex inside a liposome " *Biophysical Journal*, 96, 192-198 (2009)

[iv] C. Simon, R. Kusters, V. Caorsi, A. Allard, M. Abou-Ghali, J. Manzi, A. Di Cicco, D. Lévy, M. Lenz, J.-F. Joanny, C. Campillo, J. Plastino, P. Sens, **C. Sykes** " Actin dynamics drive cell-like membrane deformation " *Nature Physics*, https://doi.org/10.1038/s41567-019-0464-1 (2019)

[v] R. Kusters, C. Simon, R. Lopes Dos Santos, V. Caorsi, Sangsong Wu, J.-F. Joanny, P. Sens, **C. Sykes**, "Actin shells control buckling and wrinkling of biomembranes"
*Soft Matter,* **15**, 9647 – 9653 doi: 10.1039/c9sm01902b (2019)

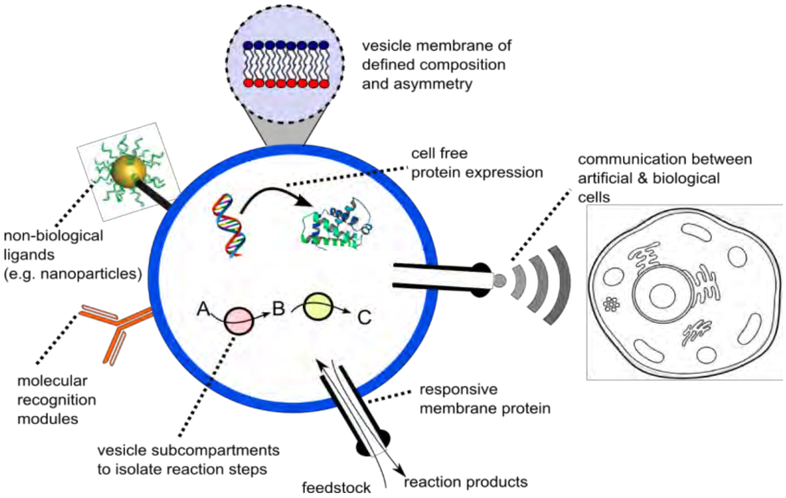
# A toolkit for artificial cell construction: droplets, opto- fluidics and biomembrane engineering

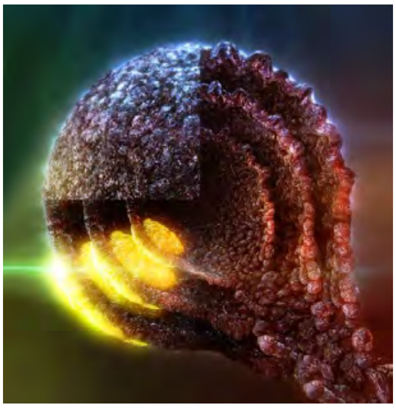
**Yuval Elani**[1]
[1] *Department of Chemical Engineering, Imperial College London, London, UK*
[2] *fabriCELL, Imperial College London, UK*

*Corresponding author:* y.elani@imperial.ac.uk

Artificial cells are cell-like entities constructed from the bottom-up using molecular building blocks, which resemble real biological cells in form and function. They are used both as simplified models of biological cells, and as smart soft-matter microdevices with a range of potential applications in industrial and clinical biotechnology. However, due to the lack of cellular infrastructure and absence of spatial organisation, the capabilities of artificial cells have not matched their biological counterparts. In this talk, I will present work from our group which aims to address this gap.

We have developed a series of technologies that allow us (i) to build cells of defined sizes, lamellarity, level of compartmentalisation, and internal architecture and (ii) to manipulate them in order to recapitulate various membranous motifs found in biology (e.g. double membranes, gap junctions, and tunnelling nanotubes). By deploying molecular bioengineering principles and by transplanting cellular machinery, we can programme our cells to possess the behaviours that are the hallmarks of life: communication, signalling, motility, sense/response, and biosynthesis. To further enhance artificial cell functionality, we use living cells and organelles as discrete functional modules that are embedded inside artificial cells. The resultant 'hybrid' cells are composed of a synthetic host and a living organelle, which enjoy a mutually beneficial relationship, and can be considered a novel living/synthetic cellular bionic material.





# Synthetic cells: De novo assembly with DNA nanotechnology

**K. Göpfrich**[1,2], K. Jahnke[1,2], Y. Dreher[1,2]
[1]*Max Planck Institute for Medical Research, Biophysical Engineering Group, Heidelberg, Germany*
[2]*Heidelberg University, Department of Physics and Astronomy, Heidelberg, Germany*

*Corresponding author: kerstin.goepfrich@mr.mpg.de*

The future of manufacturing entails the construction of biological systems and synthetic cells from the bottom up. Instead of relying exclusively on biological building blocks, the integration of new tools and new materials may be a shortcut towards the assembly of active and eventually fully functional synthetic cells [1]. This is especially apparent when considering recent advances in DNA nanotechnology and microfluidics. Exemplifying this approach, we use microfluidics for the assembly of synthetic cellular compartments that we equip with natural or DNA-based synthetic cytoskeletons [2,3]. We find that the choice of fluorophore strongly influences dynamic DNA nanostructures, which can be exploited to tune the energy landscapes for their reconfiguration [4]. We further demonstrate the division of giant unilamellar lipid vesicles (GUVs) based on osmosis and phase separation [5] or spontaneous curvature [6] rather than the biological building blocks of a cell's division machinery. We derive a parameter-free analytical model which makes quantitative predictions that we verify experimentally [5]. All in all, we believe that precision technologies, like DNA nanotechnology, can help to accelerate synthetic biology research.

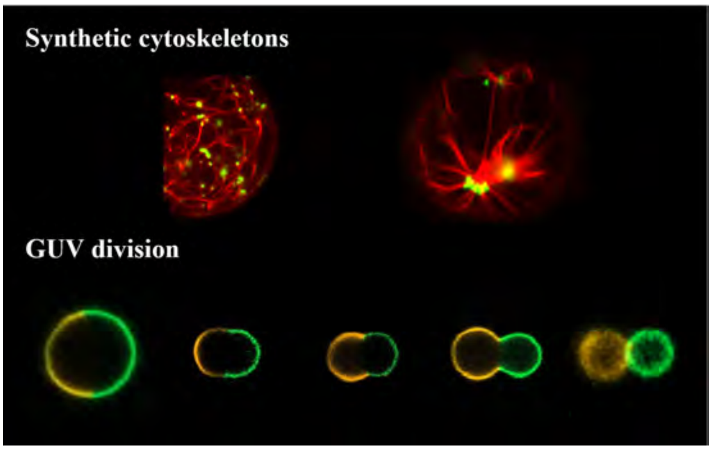


Figure 1: *Top: Confocal images of synthetic cytoskeletons inside microfluidic droplets. Bottom: Division of phase-separated GUVs.*

## References

[1] K. Göpfrich, K., I. Platzman, J. P. Spatz *Trends in Biotechnology*, **2018** 36, 938–951, DOI: 10.1016/j.tibtech.2018.03.008

[2] K. Jahnke, N. Ritzmann, J. Fichtler, A. Nitschke, Y. Dreher, T. Abele, G. Hofhaus, I. Platzman, R. Schröder, D. J. Müller, J. P. Spatz, K., Göpfrich, K. *Under review.*

[3] K. Jahnke, M. Weiss, C. Weber, I. Platzman*, K. Göpfrich*, J. P. Spatz*, *Advanced Biosystems*, **2020** 2000102, DOI: 10.1002/adbi.202000102

[4] K. Jahnke, H. Grubmüller, M. Igaev, K. Göpfrich *Nucleic Acids Research,* **2021** gkab201, DOI: 10.1093/nar/gkab201

[5] Y. Dreher, K. Jahnke, E. Bobkova, J. P. Spatz, K. Göpfrich *Angewandte Chemie,* **2020** DOI: 10.1002/anie.202014174

[6] Y. Dreher, K. Jahnke, M. Schröter, K. Göpfrich. *Under review.*

# Biomimetic curvature and tension-driven membrane fusion induced by silica nanoparticles

**M. Arribas Perez**[1,2]; P.A. Beales[1,2,3]
[1] *Astbury Centre for Structural Molecular Biology, University of Leeds, Leeds, UK*
[2] *, School of Chemistry, University of Leeds, Leeds, UK*
[3] *Bragg Centre for Materials Research, University of Leeds, Leeds, UK*
*Corresponding author: cmmap@leeds.ac.uk*

Membrane fusion is a key process to develop new technologies in synthetic biology, where artificial cells function as biomimetic chemical microreactors [1]. Fusion events in living cells are intricate phenomena that require the coordinate action of multicomponent protein complexes [2]. However, this fusion machinery essentially acts by driving a delicate balance of membrane curvature and tension between two closely apposed membranes [3]. Therefore, simpler synthetic tools able to induce such effects in lipid membranes can be employed to control membrane fusion in artificial cells.

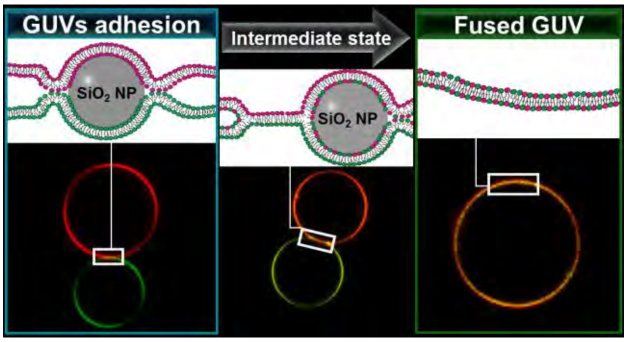


Figure 1: *Confocal microscopy images of GUVs during different stages of fusion mediated by SiO2 NPs along with a schematic representation of the potential state of the membranes at each of those stages.*

Here we show that silica nanoparticles ($SiO_2$ NPs) at a size close to the cross-over between tension-driven and curvature-driven interaction regimes initiate efficient fusion of biomimetic model membranes. Fusion efficiency and mechanisms are studied by Förster Resonance Energy Transfer (FRET) and confocal microscopy. $SiO_2$ NPs induce a slight increase in lipid packing likely to increase the lateral tension of the membrane. We observe a connection between membrane tension and fusion efficiency. In addition, real-time confocal fluorescence microscopy reveals three distinct mechanistic pathways for membrane fusion mediated by $SiO_2$ NPs. Finally, as proof-of-concept we use this system to generate phase-separated giant unilamellar vesicles (GUVs) by fusing single phased GUVs.

## References

[1] Y. Elani, R. V. Law, O. Ces *Nature Communications,* **2014** 5, 5305, DOI: 10.1038/ncomms6305

[2] N. G. Brukman, B. Uygur, B. Podbilewicz, L. V. Chernomordik *Journal of Cell Biology,* **2019** 218**,** 1436-1451, DOI: 10.1083/jcb.201901017

[3] L. V. Chernomordik, M. M. Kozlov, *Nature Structural & Molecular Biology,* **2008** 15**,** 675-683, DOI: 10.1038/nsmb.1455

# Metabolic Adaptation in DNA Protocells

**A. Samanta**,[1] V. Sabatino,[2] T. R. Ward,[2] A. Walther[1]

[1]Department of Chemistry, *Johannes Gutenberg University of Mainz, Mainz, Germany*
[2] Department of Chemistry, *University of Basel, Basel, Switzerland*

*Corresponding author: avik.samanta@uni-mainz.de*

The bottom-up approaches in designing (artificial) protocells (PC) exhibiting adaptive behaviours and downstream signal propagation are emerging challenges in synthetic biology.[1] The fundamental cellular processes (differentiation, morphogenesis, and communication) stem from numerous interwoven metabolic reaction pathways that instigate the physical changes in the periplasm in response to the external environment's trigger. The ability to mimic elementary aspects of these non-equilibrium processes in the protocells could pave the way towards designing life-like systems orchestrating complex spatiotemporal transformations. Recently, we unraveled a polymer-like phase-separation behavior in multiblock single-stranded DNA by activating a nucleobase-specific lower critical solution temperature, which provides an opportunity to fabricate all-DNA protocells with several encoded sequences for post-functionalization with spatiotemporal control.[2]

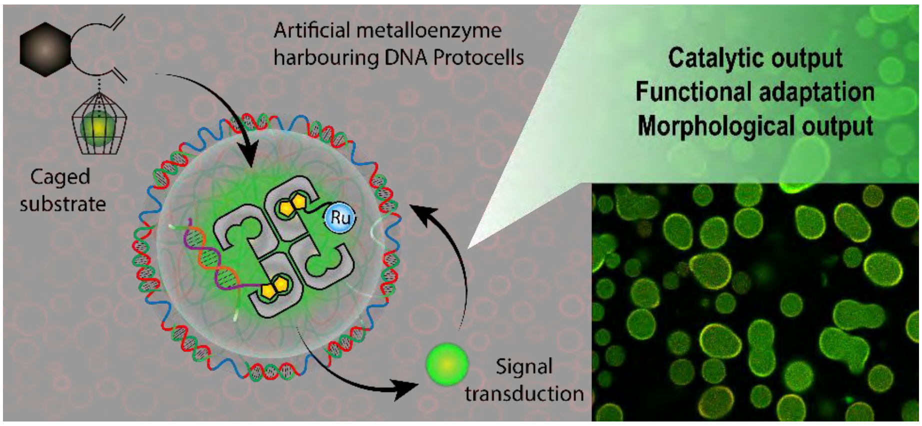


***Fig. 1.*** Artifical metalloenzyme prompted morphological and functional adapatation in all-DNA protocells.

We recently introduced the first concept for functional and morphological adaptation driven by a bioorthogonal metabolic reaction in *all*-DNA protocells (PC).[3] To achieve a metabolic transformation, we encapsulated an artificial metalloenzyme (ArM)[4] whose ring-closing metathesis activity on a pro-fluorescent substrate generated a green-fluorescent metabolite that weakened the A-T (adenine-thymine) duplexes of the PC shell by intercalation. This metabolic reaction led to PC growth, DNA mechanosensor activation, and interparticle PC fusion (Fig. 1). Genetic engineering of the metalloenzyme increased the catalytic efficiency, and significant molecular crowding effects were observed.

Even though cross-disciplinary approaches to explore the design, structure, function, and evolutionary potential of metabolic PC with genetically evolved proteinaceous catalysts are in their early stages, our approach offers valuable insights into the achievement of chemically triggered adaptive behaviour of prebiotic coacervates and towards a minimalistic design of life-like abiotic systems.

## References

1. Qiao, Y.; Li, M.; Booth, R.; Mann, S., *Nat. Chem.* **2016,** *9*, 110.
2. Merindol, R.; Loescher, S.; Samanta, A.; Walther, A., *Nat. Nanotechnol.* **2018,** *13*, 730.
3. Samanta, A.; Sabatino, V.; Ward, T. R.; Walther, A., *Nat. Nanotechnol.* **2020**, 15, 914.
4. Schwizer, F.*et. al. Chem. Rev.* **2018,** *118*, 142.

# General Session 6

Wednesday 02 June 10:40 – 12:30

# Influence of the magnetic content and short-range particle-interactions in the micro-structure and field response of colloidal magnetic brushes.

**Joan J. Cerdà** [1], Carles Bona-Casas [1], Antonio Cerrato [1], Tomàs Sintes [2], and Joan Massó [1]
[1] [a] *Dpt. de Física UIB i Institut d'Aplicacions Computacionals de Codi Comunitari (IAC3), Palma de Mallorca, Spain.*
[2] [b] *Instituto de Física Interdisciplinar y Sistemas Complejos, IFISC (CSIC-UIB). Universitat de les Illes Balears. E-07122 Palma de Mallorca, Spain.*
*Corresponding author:jj.cerda@uib.cat*

In this work we address the study of supramolecular brushes [1], whose filaments have both magnetic and non-magnetic moieties distributed along their filaments. Our study is motivated by the possibility of using these magnetic brushes as highly efficient responsive coatings that expand and contract according to an imposed external field in order to develop new types of nano-actuators. Langevin dynamics simulations have been used to study two types of brushes: sticky or Stockmayer brushes (SB) and non-sticky magnetic brushes (NSB). Our numerical results show that partially magnetic brushes have a magnetic microstructure and behaviour that in general are very different from those observed for brushes being fully magnetic, in spite of the fact that for some macroscopic observables, like magnetization, they may behave very similarly. Inside the partially magnetic class, strong differences are also observed between Stockmayer and non-sticky magnetic brushes. Results also point out that partially magnetic brushes can be much more interesting for certain purposes than their fully magnetic counterparts. These results are very promising because they show us that partially magnetic Stockmayer brushes have a great potential for applications.

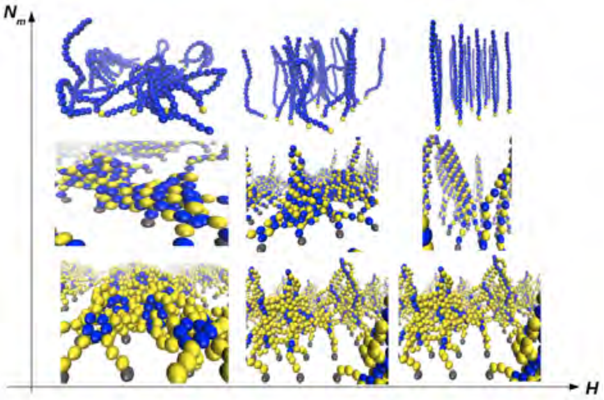


Figure 1: *Schematic diagram showing the microstructure of colloidal magnetic brushes with filaments of length* $N = 20$ *colloids as a function of the number of magnetic colloidal particles they contain,* $N_m$ *, and the external magnetic field applied,* $H$*.*

## References

[1] J. J. Cerdà, C. Bona-Casas, A. Cerrato, E. V. Novak, E. S. Pyanzina, P. A. Sánchez, S. Kantorovich and T. Sintes, *Soft Matter* **2019**, *15*, 8982–8991. DOI:

# Flow-Induced Crystallization of a Multi-Block Copolymer under Large Amplitude Oscillatory Shear: Experiments and Modelling

**G. P. Baeza[1];** M. Nébouy[1], L. Chazeau[1], J. Morthomas[1], C. Fusco[1], P. Dieudonné-George[2]

[1] *Univ Lyon, INSA-Lyon, CNRS, MATEIS, UMR 5510, 7 avenue Jean Capelle, F-69621, Villeurbanne, France*

[2] *University of Montpellier, CNRS, Laboratoire Charles Coulomb, UMR 5221, Place Eugène Bataillon, F-34095, Montpellier, France*

*Corresponding author: guilhem.baeza@insa-lyon.fr*

Following a previous work investigating the flow-induced crystallization (FIC) of PBT-PTHF multi-block copolymers under steady shear, [1] we propose here to deal with the case of large amplitude oscillatory shear (LAOS). [2] For this purpose, we focus on a single copolymer made, in average, of a sequence of nine soft- and eight hard-segments. We show unambiguously that LAOS accelerates the polymer crystallization when increasing (i) the frequency from 0.5 up to 50 rad s-1 (at constant strain amplitude of 100 %), or (ii) the strain amplitude from 10 to 300 % (at constant frequency of 2.5 rad s$^{-1}$) – see Figure 1. Based on this data, we demonstrate that high oscillatory shear rates have similar effects as the steady shear rate regarding the gelation time, i.e., that frequency and strain amplitude related effects are secondary. We carefully analyze the stress response through Fourier-Transform decomposition that emphasizes the rich rheological behavior of our material during its liquid-to-solid phase transition. With the help of X-ray scattering experiments (ex-situ SAXS and WAXS), we then propose a global scenario rationalizing the whole set of rheological observations based on the copolymer structure. In parallel, we propose to use a recent model that we developed to simulate the stress response in the case of steady shear promoted FIC and adapt it to the case of LAOS. Remarkably, our model which is based on modified Doi-Edwards equations only, provides good qualitative agreement with the data when varying the strain amplitude or the frequency. Furthermore, it is found to predict quantitatively the gelation time of the system.

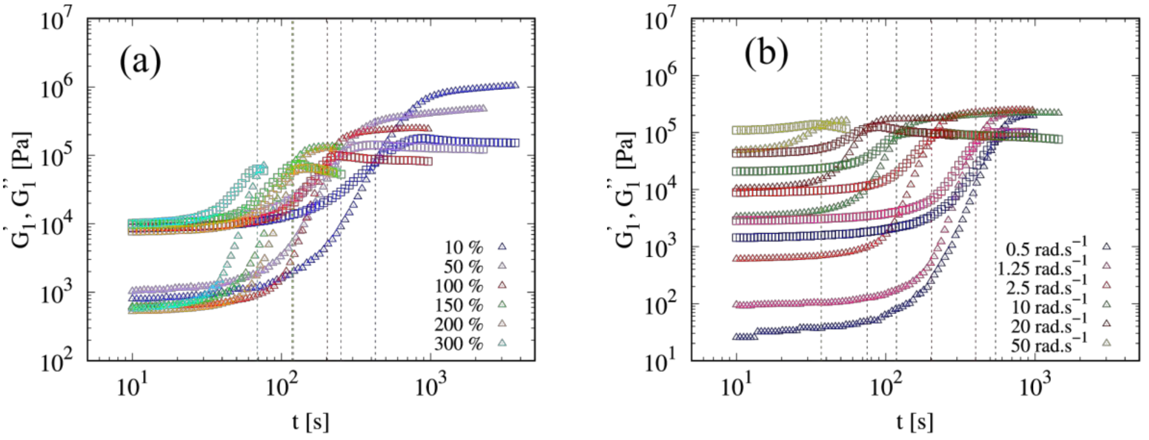


Figure 1: *Storage* ($G'_1 - triangles$) *and loss* ($G''_1 - squares$) *dynamic moduli as a function of time during the crystallization of a PBT-PTHF multi-block copolymer varying a) the strain amplitude and b) the frequency of the LAOS solicitation. [2]*

## References

[1] M. Nébouy, A. De Almeida, L. Chazeau, G.P. Baeza, *Journal of Rheology,* **2019** 63 837-850

[2] M. Nébouy, L. Chazeau, J. Morthomas, C. Fusco, P. Dieudonné-George, G.P. Baeza, *Journal of Rheology* **2021** In press

# Structure and dynamics of aqueous locust bean gum solutions

**A. M. O'Connell**[1], Y. González-Espinosa[2], F. M. Goycoolea[2], A. Gulotta[3], P. Holmqvist[3], J. Mattsson[1]
[1] *University of Leeds, School of Physics and Astronomy, Leeds, United Kingdom*
[2] *University of Leeds, School of Food Science and Nutrition, Leeds, United Kingdom*
[3] *Lund University, Division of Physical Chemistry, Lund, Sweden*
*Corresponding author: k.j.l.mattsson@leeds.ac.uk*

Locust bean gum (LBG) is a high molecular weight polysaccharide of great industrial interest due to its natural origins and strong thickening ability. In aqueous solution, LBG is known to demonstrate interesting phase behaviour such as gelation upon long-term storage or freeze-thaw cycling. However, many uncertainties remain around the solution state properties of LBG. The high molecular weight, tendency to form aggregates, and dependence on solubilisation procedure are likely causes for some of these uncertainties, and necessitate great care in characterisation.

We present a comprehensive experimental study of aqueous LBG solutions, with results obtained using steady shear rheology, static and dynamic light scattering (SLS and DLS), ultra-small-angle light scattering (USALS), and asymmetric flow field-flow fractionation (AF4) coupled to multi-angle light scattering, refractive index, and UV absorption detectors. This range of complementary techniques allows for a detailed understanding of the solution behaviour.

We identify the solutions to be mixtures of well dispersed polymer and aggregates, where the latter may be removed following a strict filtration procedure. The AF4 technique hydrodynamically separates these fractions, allowing for accurate size and molecular weight characterisation. The well-dispersed LBG is consistent with a neutral flexible polymer in good solvent conditions, while the aggregates appear highly compact and dominate the bulk solution scattering profile. The zero-shear viscosity scaling indicates three concentration regimes (dilute, semidilute unentangled, and semidilute entangled), and the intrinsic viscosity is used to determine the molecular weight, in good agreement with the value found by AF4-MALS for the dispersed polymer fraction. DLS reveals internal relaxations occurring under Zimm dynamics, apparent as a primary decay mode present at all measured concentrations. Above the entanglement concentration, a faster diffusive mode is also observed. The solution structure is probed over a wide range of lengthscales using static light scattering and USALS.

Furthermore, we determine the frequency-dependent rheology of these solutions using bulk rheometry and a range of microrheological techniques, allowing for characterisation over a broad frequency range.

Our work provides a thorough experimental characterisation of LBG solutions, revealing their behaviour over a range of concentrations from dilute to entangled regimes.

# Dynamics of hydrogels having permanent and transient crosslinks – sticky Rouse mode?

Louis DEBERTRAND, Jingwen ZHAO; Costantino CRETON; **Tetsuharu NARITA**
*Laboratoire Sciences et Ingénierie de la Matière Molle, ESPCI Paris, 75005 Paris, France.*

*tetsuharu.narita@espci.fr*

Mechanical reinforcement of hydrogels has become an important topic of the gel science. Hydrogels having simultaneously permanent crosslinks and transient crosslinks can exhibit improved mechanical properties compared to the corresponding chemical gels. These "dual crosslink" gels also show unique viscoelastic properties, while the effects of the crosslinking ratios on them have not been fully understood. In this work, in order to comprehend the dynamics of the dual crosslink gels, we synthesized model dual crosslink gels with a variable ratio of permanent and transient crosslinks, and measured their linear and nonlinear mechanical properties by both torsion and tensile tests to characterize the transient crosslinker concentration dependence, by proposing molecular interpretations of the dynamics.

Poly(vinyl alcohol) hydrogels were synthesized, with glutaraldehyde as permanent chemical (covalent) crosslinker and borate ion as transient (dynamic covalent) crosslinker. Small amplitude oscillatory shear tests (torsion tests in parallel plate geometry) and uniaxial traction tests (tensile tests) were performed. We fitted the experimental data of both torsion and tensile tests with a constitutive model to describe the dynamic properties with only four parameters.

The dynamic moduli of the dual crosslink gel can be described by (1) the low frequency elastic modulus corresponding to that of the chemical gel, (2) the high frequency elastic modulus of both permanent and transient crosslinks which are additive, (3) relaxation time of the network (at the peak of the viscous modulus) and (4) the power-law exponent of the decay in both moduli after the peak, indicating the spectrum of the relaxation time (Fig.1(a)). This power-law decay was interpreted as sticky Rouse mode, or release of the longer Rouse mode by breaking of "sticky" transient bonds. However, when the permanent and transient crosslinker concentration dependence was studied we found that the power-law exponent depends both permanent and transient crosslinkers while the relaxation time decreased with increase in the transient crosslinker concentration but independent of the permanent crosslinker concentration. We show that the power-law exponent is the function of the number of the relaxation modes, which can be defined as the number of the transient crosslinkers per permanent chain, and with increase in the number of the relaxation mode, change from Maxwell-like to Rouse-like dynamics is observed (Fig.1(b)).

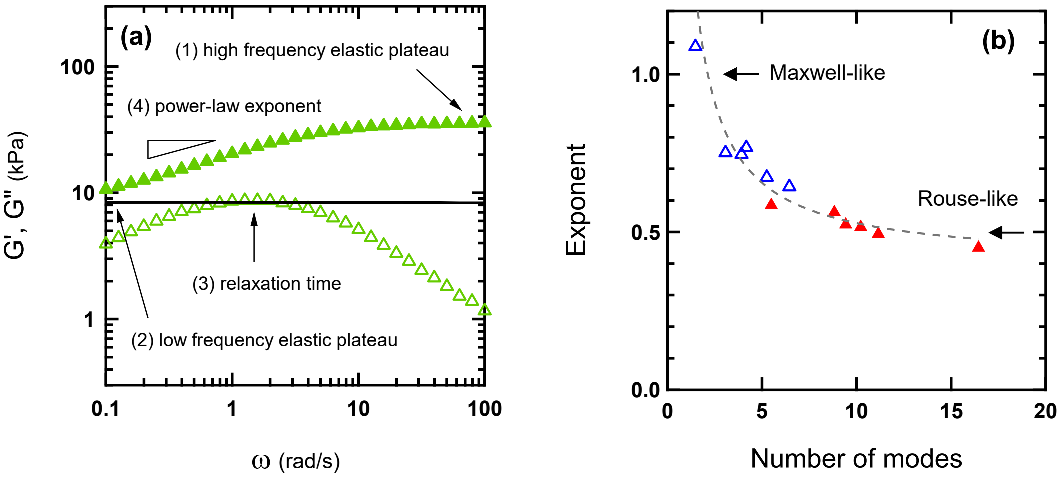


Figure 1: *(a) dynamic moduli of the dual crosslink gel. (b) Power-law exponent vs the number of modes (number of transient crosslinks per chemical chain).*

# SAXS and microfluidics as a characterization tool to study the anisotropy of lyotropic liquid crystals during flow

**A. Rodriguez-Palomo**[1], V. Lutz-Bueno[2], X. Cao[3], R. Kádár[4], M. Andersson[5], M. Liebi[1,6]

[1]*Chalmers University of Technology, Dep. of Physics, Gothenburg, Sweden.*
[2]*Paul Scherrer Institute, Swiss Light Source, Villigen, Switzerland.*
[3]*ETH Zurich, Institute for Chemical and Bioengineering, Zurich, Switzerland.*
[4]*Chalmers University of Technology, Dep. of Industrial and Materials Science, Gothenburg, Sweden.*
[5]*Chalmers University of Technology, Dep. of Chemistry and Chemical Engineering, Gothenburg, Sweden.*
[6]*EMPA, Swiss Federal Laboratories for Materials Science and Technology, Centre for X-ray Analytics, St. Gallen, Switzerland.*

*Corresponding author: adrian.rodriguez@chalmers.se*

Extrusion-based 3D printing is a promising tool to produce hierarchical structures with controlled architecture. Complex structures with high anisotropy can be created by combining additive manufacturing and self-assembled materials. Understanding these self-assembled structures under flow is a requirement to design materials with fine-tuned properties. Lyotropic liquid crystals based on block co-polymers are a good example of hierarchical materials with self-assembled structures in different length-scales. To visualize the anisotropy and nanostructure during flow inside the 3D printing nozzle, microfluidic channels were used to reproduce the nozzle geometry in combination with scanning small angle X-ray scattering (SAXS). In this study we used Pluronic-based lyotropic liquid crystals self-assembled in the hexagonal and lamellar phase, which can be used to create hierarchical composites [1,2]. The hexagonal phase showed regions with orientation perpendicular to the flow. Only in areas with shear rate higher than a threshold, an orientation in the flow direction was found. Complementary rheological measurements showed strain overshoot, which is believed to be a consequence of reoriented and ruptured structures which define a well-defined multidomain structure. For the lamellar phase a structural transition from ordered lamellae to multilamellar vesicles was observed in the scattering signal. Such transition was reversible, and the structure returned to aligned lamellae at high shear rates. These results identify the structural changes and key mechanisms of reorientation during flow, which can be expanded and applied to various similar systems [3].

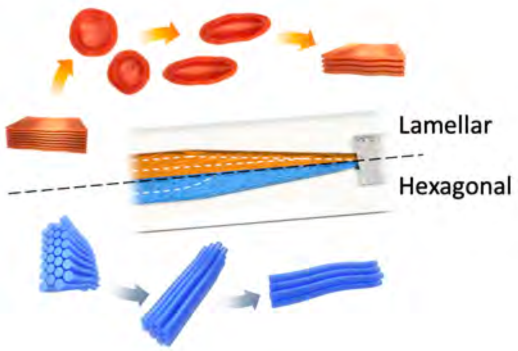


Figure 1: *Schematic illustration of the changes in the morphology and orientation of the lamellar and hexagonal self-assembled phases inside the microfluidic channels.*

## References

[1] J. Stasiak et al., Soft Matter **2014**, 10, 6077-6086, DOI: 10.1039/C4SM00884G

[2] A.K. Rajasekharan et al., Small **2017**, 13, 1700550, DOI: 10.1002/smll.201700550

[3] A. Rodriguez-Palomo et al., *Small,* **2021** 17**,** 2006229, DOI: 10.1002/smll.202006229

# General Session 7

Wednesday 02 June 15:30 – 17:20

# Control of Superselectivity by Crowding in Three-Dimensional Hosts

**H. Kusumaatmaja**[1]; A. T. R. Christy[1,2], M. A. Miller[2]
[1]*Durham University, Department of Physics, Durham, UK*
[2] *Durham University, Department of Chemistry, Durham, UK*
[1]*Institution3, Department3, City3, Country3*

*Corresponding author: halim.kusumaatmaja@durham.ac.uk*

Motivated by the fine compositional control observed in membraneless droplet organelles in cells, we investigate how a sharp binding-unbinding transition can occur between multivalent client molecules and receptors embedded in a porous three-dimensional structure. In contrast to similar superselective binding previously observed at surfaces, we have identified that a key effect in a three-dimensional environment is that the presence of inert crowding agents can significantly enhance or even introduce superselectivity [1]. In essence, molecular crowding initially suppresses binding via an entropic penalty, but the clients can then more easily form many bonds simultaneously. We demonstrate the robustness of the superselective behavior with respect to client valency, linker length, and binding interactions in Monte Carlo simulations of an archetypal lattice polymer model.

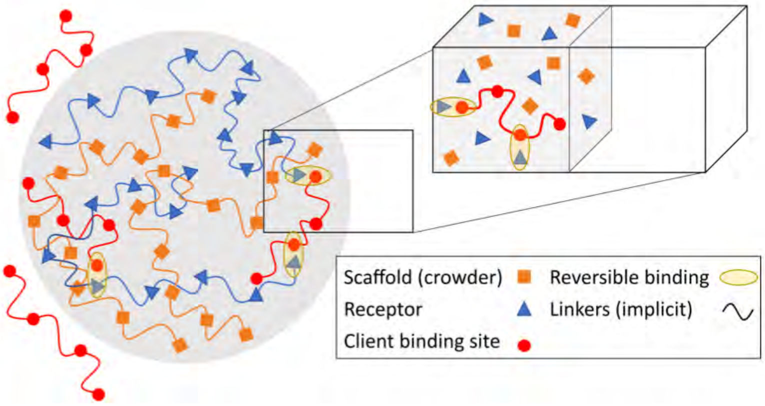


Figure 1: *Binding of multivalent clients to receptors embedded in a porous three-dimensional structure. Introducing inert crowding agents can give rise to a sharp binding-unbinding transition.*

## References

[1] A. T. R. Christy, H. Kusumaatmaja and M. A. Miller *Physical Review Letters,* **2020** 126**,** 028002, DOI: 10.1103/PhysRevLett.126.028002

# Analytical description of self-propelled polar flexible filaments

**C. A. Philipps**, G. Gompper, R. G. Winkler
*Forschungszentrum Jülich, Institute of Biological Information Processing and Institute for Advanced Simulations, Jülich, Germany*
*Corresponding author:c.philipps@fz-juelich.de*

Nature provides a variety of active matter agents, which are self-propelled units consuming either internal energy or extracting energy from their environment. The biological spectrum ranges from the macroscopic scale of a flock of birds, school of fish and mammalian herds, to self-propelled bacteria, sperm and algae, to the cellular level of the active semiflexible filaments of the cytoskeleton in living cells. In the latter, actin filaments are driven forward by myosin motors walking along the filaments [1]. This constant conversion of chemical into kinetic energy via the hydrolyzation of ATP leads to many interesting out of equilibrium phenomena. In general, active "polymers" exhibit interesting conformational and dynamical properties, even in dilute solution, which are absent in passive systems [2]. From a theoretical point of view, an analytical description of a polar active polymer is rather challenging, specifically due to the directed propulsion by the polar forces. Driving the Rouse model out of equilibrium by adding an active force tangentially to the local curvature of each monomer segment, a non-Hermitian eigenvalue problem is obtained. This transformation from a symmetric polymer to a directed A-B structure requires an adaptation of the free-ends boundary conditions and the eigenfunctions. A biorthogonal basis with respective distinct boundary conditions is established in combination with a normal mode analysis. An analytical solution of a polar filament with tangential driving forces is presented, where the filament itself is described by the Gaussian flexible polymer model [3]. It is found that the statistical properties strongly depend on the modality of applying the active force [4]. Surprisingly, conformational properties of continuous filaments are independent of activity [5]. Here, a description in terms of a discrete model has to be performed with care to avoid discretization effects. On the contrary, dynamics is activity enhanced, with the center-of-mass mean-square displacement changing from diffusion to a ballistic regime for intermediate times and back to diffusion for long times with an activity-dependent diffusion coefficient. Similarly, the decay of end-to-end vector correlation function is accelerated by activity.

## References

[1] J. Elgeti, R. G. Winkler, G. Gompper *Reports on Progress in Physics* **2015**, *78*, 056601. DOI:10.1088/0034-4885/78/5/056601

[2] R. G. Winkler, J. Elgeti, G. Gompper *Journal of the Physical Society of Japan* **2017**, *86*, 101014. DOI:10.7566/JPSJ.86.101014

[3] A. Martín-Gómez, T. Eisenstecken, G. Gompper, R. G. Winkler *Soft Matter* **2019**, *15*, 3957-3969. DOI:10.1039/C9SM00391F

[4] V. Bianco, E. Locatelli, P. Malgaretti *Physical Review Letters* **2018**, *121*, 217802. DOI:10.1103/PhysRevLett.121.217802

[5] M. S. E. Peterson, M. F. Hagan, A. Baskaran, *Journal of Statistical Mechanics: Theory and Experiment* **2020**, *2020*, 013216. DOI:10.1088/1742-5468/ab6097

# Unravelling Nature's Networks:
# Control of intra-protein nano-staples defines architecture and mechanics of protein networks due to *in situ* unfolding

**Matt D G Hughes**[1], Benjamin S Hanson[1,2], Sophie Cussons[2,3], Najet Mahmoudi[4], David J Brockwell[2,3], *Lorna Dougan*[1,2]

1 School of Physics and Astronomy, University of Leeds, UK
2 Astbury Centre for Structural Molecular Biology, University of Leeds, UK
3 School of Molecular and Cellular Biology, Faculty of Biological Sciences, University of Leeds, UK
4 ISIS Neutron and Muon Spallation Source, STFC Rutherford Appleton Laboratory, UK
Corresponding Author*: Lorna Dougan, L.Dougan@leeds.ac.uk*

Hierarchical assemblies of semi-flexible biopolymers, such as proteins, exhibit a wide-range of material properties that are exploited both in nature and by mankind. Recent work has focused on understanding the importance of the building block stability[1], however little is understood about the importance of the transition from the protein's native folded state to its unfolded state in network assembly. To determine the importance of *in situ* unfolding on network properties we control the force lability of a single protein building block, by reducing the natively disulphide reinforced bovine serum albumin (BSA).[2]

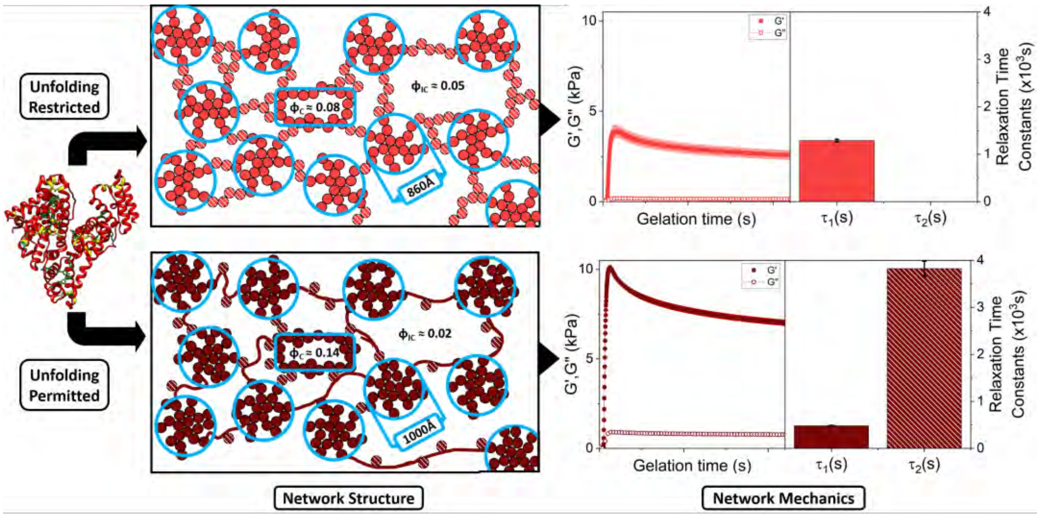


Figure 1: (left) Crystal structure of BSA (PDB code: 3V03). (middle) Predicted network architectures of BSA hydrogels in the (top) absence and (bottom) presence of the reducing agent DTT. (right) Gelation curves of BSA hydrogels showing storage and loss moduli as a function of gelation time and the extracted of post-photo-chemical cross-linking relaxation time constants in the (top) absence and (bottom) presence of DTT (where $\tau_1$ and $\tau_2$ relaxations are attributed to network rearrangement and *in situ* unfolding respectively).

Employing a combination of circular dichroism spectroscopy, small-angle scattering, rheology and modelling we show that restricting unfolding leads to homogeneous networks of cross-linked fractal-like clusters connected by an inter-cluster region of folded protein. Conversely, allowing in situ unfolding results in more heterogeneous networks of denser fractal-like clusters connected by an inter-cluster region populated by unfolded protein. In addition, gelation-induced protein unfolding and crosslinking in the inter-cluster region changes the hydrogel mechanics, as measured by a 3-fold enhancement of the storage modulus, an increase in both the loss ratio and energy dissipation, and markedly different relaxation behaviour. By controlling the protein's ability to unfold through nanoscale stapling, we demonstrate the importance of in situ unfolding in defining both network architecture and mechanics, providing insight into fundamental hierarchical mechanics and a novel route to tune biomaterial for future applications.

## References:

1 **M. D. G. Hughes**, S. Cussons, N. Mahmoudi, et al., *Soft Matter*, 2020, **16**, 6389–6399.

2 **M. D. G. Hughes**, B. S. Hanson, S. Cussons, N. Mahmoudi, et al., *ACS Nano (Under Rev.)*.

# On the interaction of β-glucosidase with Wrinkled $SiO_2$ nanoparticles: the protein corona formation

**G. Pota**[1]; D. Cavasso[2]; I. Russo Krauss[2,3]; V. Califano[4]; L. Paduano[2,3]; A. Costantini[1]; G. Vitiello[1,3]

[1]*University of Naples Federico II, Department of Chemical, Materials and Production Engineering, Naples, Italy*
[2]*University of Naples Federico II, Department of Chemical Sciences, Naples, Italy*
[3]*CSGI, Center for Colloid and Surface Science, Sesto Fiorentino (FI), Italy*
[4]*Istituto di Scienze e Tecnologie per l'Energia e la Mobilità Sostenibili STEMS-CNR, Naples, Italy*

*Corresponding author:* giulio.pota@unina.it

β-Glucosidase (BG) is an enzyme involved in the conversion of lignocellulosic biomass to obtain biofuel. It catalyzes the hydrolysis of cellobiose into glucose, which can be fermented to produce bioethanol. However, BG is costly, slightly thermally unstable at the reaction operative conditions as well as difficult to rescue from the reaction environment. Enzyme immobilization onto solid supports helps overcome these issues [1]. In this context, Wrinkled Silica Nanoparticles (WSN), a type of nanoparticles with central-radial pore structure [2], represent an ideal support for BG immobilization (Fig. 1a, 1b). The aim of the present study is to investigate the interaction mechanism of BG with WSN, unveiling the relationship between the enzyme organization onto the WSN surface and the catalytic performance. Herein, the kinetics of immobilization at different support-to-enzyme ratios were investigated by Dynamic Light Scattering (DLS), Circular Dichroism (CD) and Fourier Transform Infrared Spectroscopy (FTIR). DLS results showed that a 6:1 support-to-enzyme ratio provides the highest colloidal stability for the biocatalyst. CD spectra (Fig. 1c) assessed that the protein retains almost completely its structure during the process of adsorption as confirmed by the deconvolution of Amide I band (1650 $cm^{-1}$) in the FTIR spectrum of the sample [3]. Moreover, CD intensity decreases with time, likely because the protein gets inside the pore structure and its shielded from UV rays by the silica skeleton of the nanoparticles. Thermal denaturation curves of free and immobilized enzymes were compared indicating that the supported biocatalyst experiences no denaturation, whereas half the protein in its free form is denatured at 74 °C. Finally, immobilized biocatalyst exhibits a full activity with respect to the free enzyme in the hydrolysis of cellobiose to glucose.

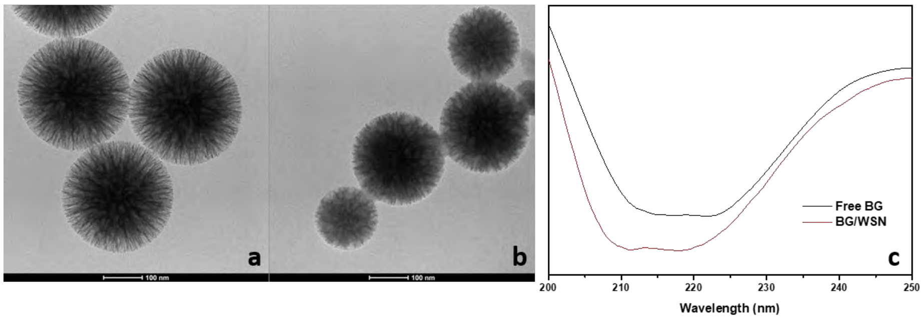


**Figure 1:** TEM images of bare WSN (**a**) and BG-immobilized WSN (**b**). CD spectra of free and immobilized BG onto WSN surface (**c**).

## References

[1] Nguyen, H. H. et al. *Applied Science and Convergence Technology*, **2017**, *26*, 157-163, DOI:10.5757/ASCT.2017.26.6.157

[2] Califano, V. et al. *The Journal of Physical Chemistry C*, **2018**, *122*, 8373, DOI: 10.1021/acs.jpcc.8b00652

[3] Perez-Pons, J. A. et al. *Biochemical Journal*, **1995**, 308,791-794, DOI:10.1042/bj3080791

# Self-assembly of alternated lipo/hydrophilic copolymers in water: domain of occurrence and structure of the ouzo phase.

**H. Trevisan**[1]; F. Tournilhac[1]

[1]*ESPCI-Paris, Molecular, Macromolecular Chemistry, and Materials Lab, UMR 7167, Paris, France*

*Corresponding author: francois.tournilhac@espci.fr*

Selection of monomer couples, ensuring reactivity ratios close to zero, is an effective strategy to induce spontaneous copolymerization into an alternated sequence.[1,2] In addition, monomer design and customization of the solvent-monomer interactions opens the way to functional copolymers showing molecular self-assembly relevant to their regular amphipathic structure.[2] In this work, we show that the design of comonomers with adequate reactivities and interactions can be used to direct copolymer self-assembly on a mesoscopic scale. We investigate spontaneous formation of nanoparticles through solvent/non-solvent interaction using the so-called "ouzo effect". In this way, an ouzo diagram was built to determine the operation window for the self-assembly of alternated copolymers consisting of vinyl phenol and maleimide units carrying long alkyl-pendant groups ($C_{12}H_{25}$ or $C_{18}H_{37}$) in aqueous solutions (Figure 1). Also, investigations were pursued to account the influence of the lateral lipophilic pendant units on the size and structure of the nanoaggregates formed during one-shot water addition. Structure characterization by light scattering techniques (DLS and SLS), small-angle neutron scattering (SANS) and cryogenic transmission electron microscopy (Cryo-TEM) confirms the self-assembly of copolymer chains into nanoparticles (hydrodynamic radius range: 60 – 300 nm), which size is affected by the lipophilicity of the alternating copolymers and the solvent diffusion in water. Altogether, we present here the spontaneous ouzo effect as a simple method to produce stable alternating copolymer nanoparticles in water without the addition of stabilizing agents.

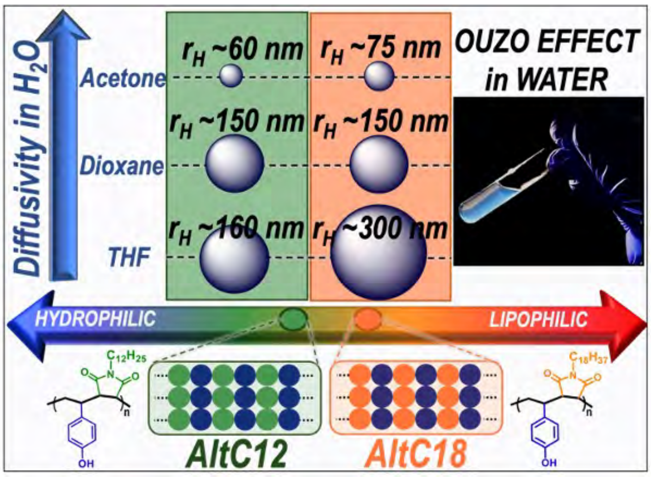


Figure 1: *Lateral alkyl pendant-groups ($C_{12}H_{25}$ or $C_{18}H_{37}$) on sequence alternated copolymers (AltC12 and AltC18, respectively) confers tuneable lipophilicity, allowing the spontaneous formation of nanoparticles in aqueous suspension with different sizes and structures, that vary with solvent diffusion in water.*

## References

[1] K. Nishimori, M. Ouchi, *ChemComm,* **2020** 56**,** 3473, DOI: 10.1039/d0cc00275e

[2] K. Nishimori, E. Cazares-Cortes, J-M. Guigner, F. Tournilhac, M. Ouchi, *Polymer Chemistry,* **2019** 10**,** 2327, DOI: 10.1039/c9py00329k

# General Session 8

Wednesday 02 June 15:30 – 17:20

# Can the roles of polar and non-polar moieties be reversed in non-polar solvents?

**C. J. Dongmo Foumthuim** [1], M. Carrer[2], M. Houvet[3], T. Škrbić[1,4], G. Graziano[5],
A. Giacometti[1,6]
[1] *Università Ca' Foscari di Venezia, Dipartimento di Scienze Molecolari e Nanosistemi, Venezia Mestre, Italy*
[2] *University of Oslo, Department of Chemistry and Hylleraas Centre for Quantum Molecular Sciences, Oslo, Norway*
[3] *Polytech Nantes-Engineering School of the University of Nantes, Nantes Cedex 3, France*
[4] *University of Oregon, Department of Physics and Institute for Fundamental Science, Eugene, USA*
[5] *University of Sannio-Benevento, Department of Science and Technology, Benevento, Italy*
[6] *6European Centre for Living Technology (ECLT), Venice, Italy*
*Corresponding author:cedrix.dongmo@unive.it*

Using thermodynamic integration, we study the solvation free energy of 18 amino acid side chain equivalents in solvents with different polarities, ranging from the most polar water to the most non-polar cyclohexane. The amino acid side chain equivalents are obtained from the 20 natural amino acids by replacing the backbone part with a hydrogen atom, and discarding proline and glycine that have special properties. A detailed analysis of the relative solvation free energies suggests how it is possible to achieve a robust and unambiguous hydrophobic scale for the amino acids (see Fig.1 below). By discriminating the relative contributions of the entropic and enthalpic terms, we find strong negative correlations in water and ethanol, associated with the well-known entropy-enthalpy compensation, and a much reduced correlation in cyclohexane. This shows that in general the role of the polar and non-polar moieties cannot be reversed in a non-polar solvent. Our findings are compared with past experimental as well as numerical results, and may shed additional light on the unique role of water as a biological solvent.

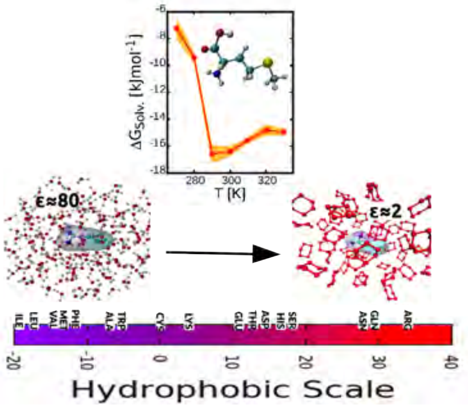


Figure 1: *Temperature dependence of the solvation free energy of methyl-ethylsulfide (methionine) in cyclohexane. The graph further exemplifies the transfer free energy of the latter analyte from a polar solvent, water ($\epsilon \approx 80$) to a non-polar solvent, cyclohexane ($\epsilon \approx 2$). This scheme is demonstrated to provide a robust and unambiguous classification of the relative hydrophobicity scale of amino acids, which indeed includes both physicochemical properties of solvent and solute. The hydrophobic scale suggested by this study is finally displayed on the bottom of the graph.*

## References

[1] C.J. Dongmo Foumthuim, M. Carrer, M. Houvet, T. Škrbić, G. Graziano, and A. Giacometti *Phys. Chem. Chem. Phys.* **2020**, *22*, 25848 - 25858. DOI:10.1039/D0CP02948C

# Cyclic Polyethylene Glycol as Nanoparticle Surface Ligand

**Fabienne Barroso-Bujans**[1,2,3], Mohammad A. Aboudzadeh[1,3], Marek Grzelczak[1,3]
[1]*Donostia International Physics Center, Donostia-San Sebastian, Spain*
[2]*IKERBASQUE - Basque Foundation for Science, Bilbao, Spain*
[3]*Materials Physics Center, CSIC-UPV/EHU, Spain*

*Corresponding author: fbarroso@dipc.org*

Cyclic polymers behave dramatically different than linear polymers due to the lack of end groups and smaller coil dimensions. We demonstrate that cyclic polyethylene glycol (PEG) can be used as an alternative of classical linear PEG ligands for gold nanoparticle (AuNP) stabilization. To this aim, we introduced a synthetic approach to synthesize cyclic PEG chemically attachable to gold surfaces [1]. Then, cyclic PEG was chemically attached to AuNPs by using standard ligand exchange procedures and the colloidal stability of nanoparticles evaluated [2]. Our results showed that the brush height of cyclic PEG increases identically as that of linear brushes in water with $(N\sigma^{1/2})^{0.7}$ (N, chain length and $\sigma$, grafting density) suggesting more extended conformations in the cyclic chains. Such structural effect and the reduced footprint diameter in cyclic brushes helped to explain the distinct response of AuNPs to ionic strength and temperature, respectively, compared to linear analogues.

Our latest studies on the colloidal stability of AuNPs modified with cyclic PEG were performed in ethanol, a solvent where neat PEG exhibit a non-conventional upper critical solution temperature. We observed that linear PEG brushes cause the precipitation of AuNPs (13 nm diameter) in hours without altering their surface plasmon resonance in a non-conventional temperature-reversible process. However, when the polymer brush topology is cyclic the precipitation is avoided while providing a very high colloidal stability to AuNPs in ethanol at -25 ºC for days. We postulated a mechanism where a fast reversible collapse of chain brushes leads to a state that is favorable for the interpenetration of linear chains and precipitation of AuNPs in a slow process, but which is not favorable for the interpenetration of cyclic polymer brushes. Our results evidence that the topology of PEG brushes plays an important role on the colloidal stability of AuNPs.

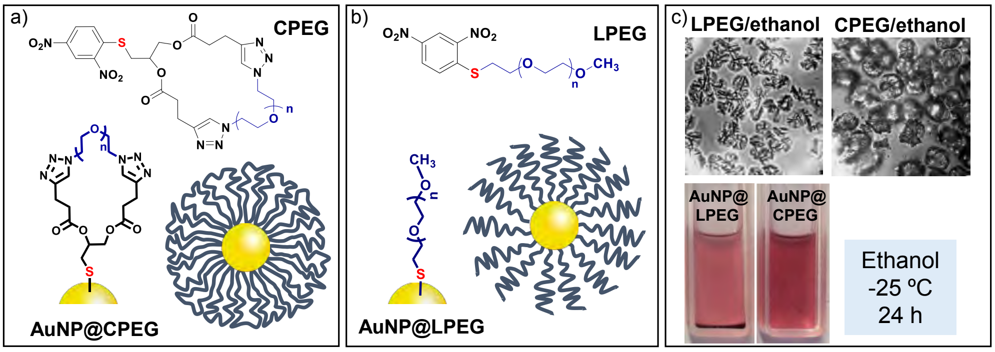


Figure 1: *Gold nanoparticles stabilized with PEG of different topologies. Structure of a) cyclic PEG (CPEG) and b) linear PEG (LPEG) with protected thiol groups. c) Optical microscopy of neat polymers in ethanol at -10 ºC and pictures of AuNPs modified with CPEG and LPEG in ethanol, stored at -25 ºC overnight.*

## References

[1] M. A. Aboudzadeh, M. Dolz, X. Monnier, E. González de San Román, D. Cangialosi, M. Grzelczak, F. Barroso-Bujans, *Polym. Chem.* **2019**, *10*, 6495

[2] M. A. Aboudzadeh, A. Iturrospe, A. Arbe, M. Grzelczak, F. Barroso-Bujans, *ACS Macro Lett.* **2020**, *9*, 1604

# Swimming behavior of squirmer dumbbells and polymers

**J. Clopés**, G. Gompper, R. G. Winkler
*Forschungszentrum Jülich, Theoretical Soft Matter and Biophysics, Institute for Advanced Simulation and Institute of Biological Information Processing, Jülich, Germany*
*Corresponding author: r.winkler@fz-juelich.de*

Nature provides a plethora of microswimmers, which can be rather elongated, filament- or polymer-like [1, 2]. Examples are bacteria swarmer cells or marine phytoplankton dinoflagellates assembling in a linear fashion. In order to address the relevance of hydrodynamic interactions for the collective behavior of such organisms, we study the swimming properties of linear polymer-like assemblies by mesoscale hydrodynamic simulations, where an active unit (monomer) is described by a spherical squirmer – which can be a pusher, a neutral swimmer, or a puller. We find that the monomer hydrodynamic flow field leads to correlations in the relative orientation of adjacent monomers (see Figure 1), and consequently the swimming efficiency differs from that of active Brownian linear assemblies. In particular, puller dumbbells and chains show a pronounced increase in the rotational diffusion coefficient compared to pushers, while for neutral squirmers, the rotational diffusion coefficient is similar to that of active Brownian particles [3]. Hence, the large-scale conformational and dynamical properties depend on the specific propulsion mechanism.

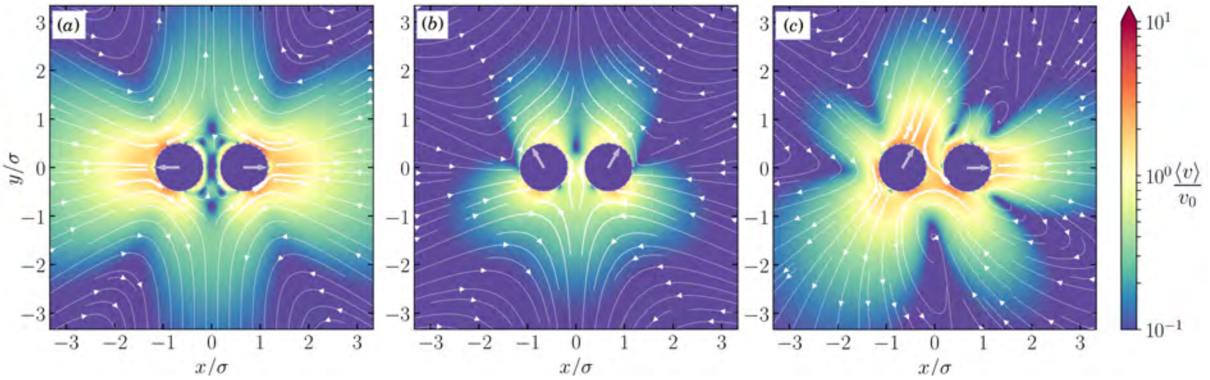


Figure 1: *Flow fields in the laboratory reference frame of most probable squirmer-squirmer relative orientations in dumbbells for different active stresses, $\beta$, (a) pullers ($\beta = 5$), (b) weak pushers ($\beta = -1$), (c) strong pushers ($\beta = -5$).*

## References

[1] J. Elgeti, R. G. Winkler, G. Gompper *Rep. Prog. Phys.* **2015**, *78*, 056601. DOI:10.1088/0034-4885/78/5/056601

[2] R. G. Winkler, J. Elgeti, G. Gompper *J. Phys. Soc. Jpn.* **2017**, *86*, 101014. DOI:10.7566/JPSJ.86.101014

[3] J. Clopés, G. Gompper, R. G. Winkler *Soft Matter* **2020**, *16*, 10676. DOI:10.1039/d0sm01569e

# Structure and dynamics of supramolecular model polymer: influence of polymer polarity and association strength

**Ana Brás**[1]; Ana Arizaga,[1] Uxue Agirre,[1] Marie Dorau,[1] Daria Sokolova,[1,2] Judith E. Houston,[3,4] Aurel Radulescu,[4] Sylvain Prévost[5], Margarita Kruteva[6], Wim Pyckhout-Hintzen[6], Annette M. Schmidt[1]
[1]*Institute of Physical Chemistry, University of Cologne, Cologne, Germany*
[2]*Chemistry Department, University of Basel, Basel, Switzerland*
[3]*European Spallation Source ERIC , Lund, Sweden*
[4]*Jülich Centre for Neutron Science (JCNS) at Heinz Maier Leibnitz-Zentrum (MLZ), Forschungszentrum Jülich GmbH, Munich, Germany*
[5]*Institut Laue-Langevin, Life Sciences Group, Grenoble, France*
[6]*Jülich Centre for Neutron Science (JCNS-1) and Institute for Complex Systems (ICS-1), Forschungszentrum Jülich GmbH, Jülich, Germany*

*Corresponding author: aeliasbr@uni-koeln.de*

Supramolecular polymers, in which non-covalent interactions such as hydrogen bonds or metal coordination keep the repeating units together, offer exciting prospects for materials with novel properties because of the reversibility of the interactions [1]. This new class of materials combines the overall good chemical and mechanical properties of polymers with inherent dynamic reversible supramolecular interactions. Amongst others, hydrogen bonding (H-bonding) represents such a reversible mechanism [2]. The presented work focuses on the self-assembly of polymer model systems in the bulk via H-bonding. Our investigations are based on polymers with either a polypropylene oxide (PPO) or a polyethylene oxide (PEO) backbone, respectively. Diaminotriazine (Dat) and Thymine-1-acetic acid (Thy), as well as 2-ureido-4[1H]-pyrimidinone (Upy) are used as covalently attached functional end groups. Different experimental techniques such as small angle scattering and rheology were combined to study in particular the correlation between the backbone polarity and the different end-groups association strength as Upy is highly self-associative [1,2] in comparison to the heterocomplementary pair Thy/Dat. Results on the structure show that PEO and PPO functionalized with the pair Thy/Dat self-assemble as linear chains [3], while both polymers functionalized with Upy show a sphere-particle morphology corresponding to a Upy rich-phase. The corresponding Upy cluster radius is larger on PEO than on PPO due to the higher chain hydrophilicity. This means that the bonding energy is affected by the different polarities. An analysis of the dynamical behavior indicates not only the formation of a supramolecular network, but also a dramatically change from a typical Newtonian fluid behavior as observed for Thy/Dat groups.

*Acknowledgment:*

A.B. acknowledges DFG for a research grant (BR5303). A.B thanks Prof. Dr. D. Richter and Prof. Dr. R. Strey for fruitful discussions.

**References**

[1] J. Cortese, C. Soulie-Ziakovic, S. Tence-Girault, L. Leibler *JACS*, **2012** 134, 8, 3671; J. H. K. Ky Hirschberg, A. Ramzi, R. P. Sijbesma, E. W. Meijer *Macromolecules*, **2003** 36, 1429; F. Herbst, W. H. Binder *Polymer Chemistry*, **2013** 4, 3602.

[2] R. P. Sijbesma, F. H. Beijer, L. Brunsveld, B. J. B. Folmer, J. H. K. K. Hirschberg, R. F. M. Lange, J. K. L. Lowe, E. W. Meijer, *Science*, **1997** 278,160.

[3] A. R. Brás, C. H. Hövelmann, W. Antonius, J. Teixeira, A. Radulescu, J. Allgaier, W. Pyckhout-Hintzen, A. Wischnewski, D. Richter, *Macromolecules*, **2013** 46, 9446. M. Krutyeva, A. R. Brás, W. Antonius, C. H. Hövelmann, A. S. Poulos, J. Allgaier, A. Radulescu, P. Lindner, W. Pyckhout-Hintzen, A. Wischnewski, D. Richter, *Macromolecules*, **2015** 48, 8933.

# A Natural, Cellulose-Based Microgel for Water-in-Oil Emulsions

**K.S. Lefroy**[1]; B.S Murray[1], M. E. Ries,[2] T. D. Curwen[3]
[1]*University of Leeds, School of Food Science and Nutrition, Leeds, UK*
[2]*University of Leeds, School of Physics and Astronomy, Leeds, UK*
[3]*Mondelēz International, Reading Science Centre, Reading, UK*

*Corresponding author: fskl@leeds.ac.uk*

Non-derivatised cellulose is generally assumed to have poor surface activity and therefore be unsuitable as a water in oil (W/O) emulsifier. In this work, a "natural" cellulose microgel (CMG) is fabricated via a top-down approach and used to stabilise W/O emulsions, without employing chemical modification. The cellulose is coagulated from an ionic liquid through a solvent-exchange process, in the presence and absence of added sunflower oil, in order to tune the cellulose morphology and properties. Detailed characterization of the nature of these microgels and the effect of the solvent change sequence on their emulsifying properties was investigated.

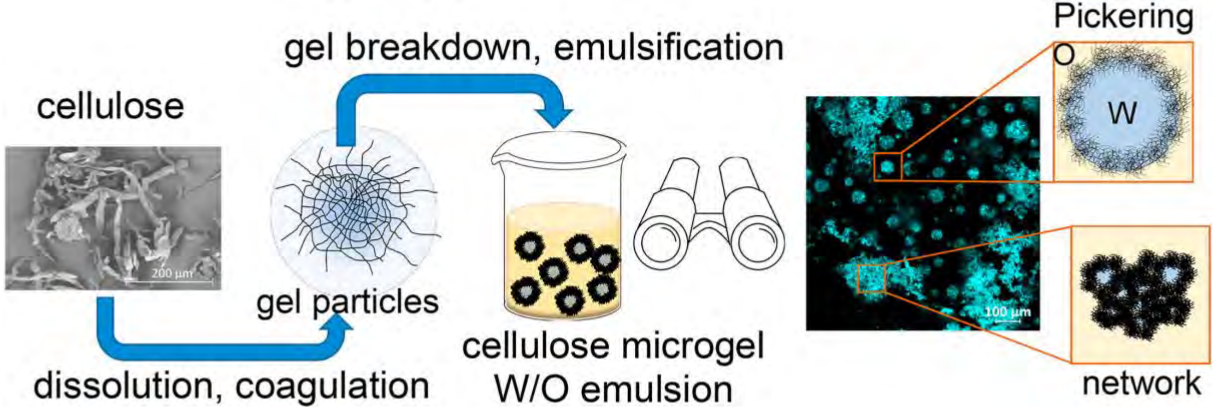


Figure 1: *Process of fabricating cellulose microgels (CMG) via coagulation from an ionic liquid. CMGs are then used to form water-in-oil (W/O) emulsion, through Pickering and network stabilisation .*

In the presence of oil, Fourier transform infrared (FTIR) spectroscopy confirmed the retention of oil in the coagulum during regeneration and the resultant CMGs were more easily dispersed in oil than water, suggesting the fabrication of a "hydrophobic" microgel. Confocal microscopy confirmed the adsorption of CMGs to the water-oil interface and W/O emulsions of up to 20 wt.% water displayed good stability over at least 1 month. This study therefore describes a "novel" route to W/O stabilisation using a natural emulsifier, which could be then used as a method of reducing fat and sugar in food products.

## References

[1] K. S. Lefroy, B. S. Murray, M. E Ries and T. D Curwen, *Food Hydrocolloids,* **2021** 113**,** 106408, DOI: 10.1016/j.foodhyd.2020.106408

# Poster Session 3

Wednesday 02 June 14:00 – 15:30

# Kinetics of network formation and heterogeneous dynamics of an egg-white gel revealed by coherent X-ray scattering

**Nafisa Begam**[1], Anastasia Ragulskaya[1], Anita Girelli[1], Hendrik Rahmann[2], Sivasurender Chandran[3], Fabian Westermeier[4], Mario Reiser[2,5], Michael Sprung[4], Fajun Zhang[1], Christian Gutt[2], and Frank Schreiber[1]

[1] Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen, Germany
[2] Department Physik, Universität Siegen, 57072 Siegen, Germany
[3] Department of Physics, Indian Institute of Technology Kanpur, Kanpur, Uttar Pradesh 208016, India
[4] Deutsches Elektronen-Synchrotron DESY, Notkestrasse 85, 22607 Hamburg, Germany
[5] European X-ray Free-Electron Laser GmbH, Holzkoppel 4, 22869 Schenefeld, Germany

*Corresponding author: nafisa.begam@ifap.uni-tuebingen.de*

Gelation of proteins, e.g. egg-white, is a fundamental topic in food chemistry as well as in condensed matter physics [1,2]. Naturally, it draws a lot of attention of the scientific communities. However, our understanding on the kinetics of network formation and the microscopic dynamics, especially at the length scales of the mesh size of the network, is limited due to the experimental difficulties at accessing those length and corresponding time scales. Here, using state-of-the-art X-ray photon correlation spectroscopy [3,4] along with ultra-small angle X-ray scattering, we probe the kinetics of heat-induced gelation and the microscopic dynamics of a hen egg-white gel. Kinetics of structural growth reveals a reaction-limited aggregation process with a gel fractal dimension of ~ 2 and an average network mesh size of ca: 400 nm [5].

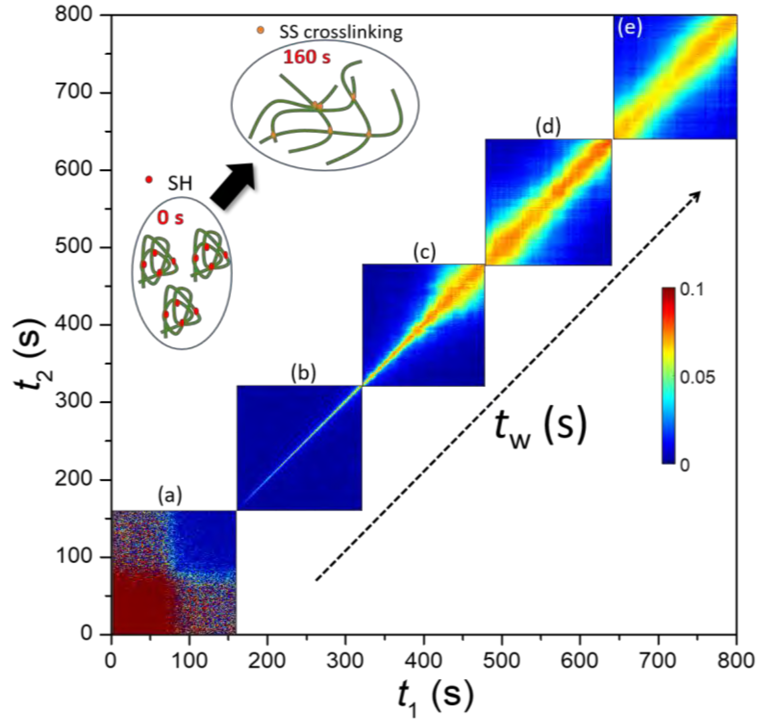


Figure 1: *TTC (CI -1) collected at 80°C (at $q = 0.01\ \mathrm{nm}^{-1}$) in the time interval of (a) 0-160 s, (b) 160-320 s, (c) 320-480 s, (d) 480-640 s and (e) 640-800 s after reaching the temperature. Inset schematic shows the native state of the proteins before denaturation (0 s after heating at 80°C) and after unfolding due to heat denaturation (160 s after heating at 80°C).*

Dynamics probed at these length scales reveal two distinct regimes after the establishment of the network structure as can be seen in figure 1. While the first regime of the dynamics is characterized by an exponential growth of the characteristic relaxation times (until $t_w$ = 480 s after heating at 80 ºC), the second regime is characterized by an intriguing steady state and temporally heterogeneous dynamics [5]. The intermediate scattering function changes from an exponential to a compressed exponential decay. We deduce wave vector $q$-dependent fourth order intensity correlation functions to quantify the observed heterogeneity. The degree of heterogeneity increases with increasing $q$. We identify the stress-driven dynamics as dynamical rupture events which do not change the structure of the gel. The spatial extension of these decorrelation events decreases from 100 nm to a few nm upon aging accompanied by a lowering of the degree of dynamical heterogeneity. We discuss our results in the broader context of experiments and models describing attractive colloidal gels. Our findings help to understand the transformation of a real protein system to a heat-induced solid-like gel-state and the underlying dynamical transition that dictates the characteristic properties of the gel.

## References

[1] V. Raikos, L. Campbell, and S. R. Euston, *Food Hydrocoll.* 21, 237 (2007).
[2] M. Fach, L. Radi, and P. R. Wich, *J. Am. Chem. Soc.* 138, 14820 (2016).
[3] H. Conrad, F. Lehmkühler, B. Fischer, F. Westermeier, M. A. Schroer, Y. Chushkin, C. Gutt, M. Sprung, and G. Grübel, *Phys. Rev. E* 91, 042309 (2015).
[4] S. K. Sinha, Z. Jiang, and L. B. Lurio, *Adv. Mater.* 26, 7764 (2014).
[5] N Begam, A Ragulskaya, A Girelli, R Hendrik, S Chandran, F Westermeier, M Reiser, M Sprung, F Zhang, C Gutt, And F Schreiber, *Phys. Rev. Lett* (2021), 126, 098001.

# Linear viscoelasticity of supramolecular bis-urea based polymers at high pressures and temperatures

N. A. Burger[1,2], G. Meier[3], L. Bouteiller[4], B. Loppinet[1], D. Vlassopoulos[1,2]

1 Foundation for Research & Technology Hellas (FORTH), Institute for Electronic Structure & Laser, Heraklion 70013, Greece

2 University of Crete, Department of Materials Science & Technology, Heraklion 70013, Greece

3 Forschungszentrum Jülich, Institute of Complex Systems (ICS-3), 52425 Jülich, Germany

4 Sorbonne Université, CNRS, IPCM, Equipe Chimie des Polymères, 75005 Paris, France

*Corresponding author:* burker@materials.uoc.gr

The monomer, 2,4-bis(2-ethylhexylureido)toluene (EHUT), self-assembles through hydrogen bonding when immersed in non-polar solvents. Two distinct supramolecular structures have been reported, tubes and filaments (depending on solvent conditions), which are characterized by viscoelastic and viscous behaviour, respectively. Here we report on the effects of high hydrostatic pressure (HHP) on the structures and the (micro)rheology of EHUT solutions in cyclohexane and dodecane. We combine dynamic light scattering (DLS) and passive probe microrheology under HHP. The HHP is obtained by pressurizing a stainless steel chamber by means on an inert gas. The DLS-based probe microrheology provides the linear viscoelastic spectrum over a wide range of frequencies.

The tube to filament transition is identified through strong variation of the viscoelasticity and the scattered intensity. We find that HHP stabilizes the tube structures both in cyclohexane [1] (fig. 1) and in dodecane. We investigate the effect of temperature and concentration on the viscoelastic spectrum, evidencing large variation of the dynamic viscosities. In particular, in dodecane solutions at atmospheric pressure we observe the presence of viscous (unentangled) tube phase at low concentrations (below 3 g/L). The results allow us to build a state diagram in the temperature-concentration space. The influence of the different parameters is discussed including the possible role of dissolved residual water.

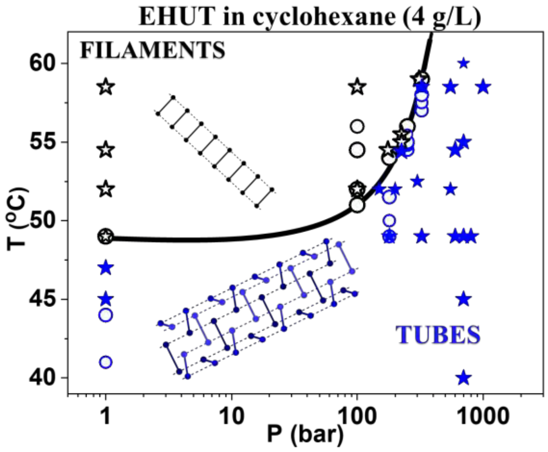


Figure 1: *Phase diagram of a 4 g/L EHUT / cyclohexane solution in the (T, P) space. Star symbols correspond to passive microrheological data. Circles correspond to DLS (without added particles). The black line is drawn to guide the eye. Blue (black) color indicates tubes (filaments).*

## References

[1] N. A. Burger, A. Mavromanolakis, G. Meier, P. Brocorens, R. Lazzaroni, L. Bouteiller, B. Loppinet, and D. Vlassopoulos, ACS Macro Letters, *2021, 10, 3, 321–326.* DOI: 10.1021/acsmacrolett.0c00834

# Linear and non-linear rheology of dynamic gels

**A. Chaub**[1]; M. Cloitre[1]

[1]*ESPCI Paris, Chimie Moléculaire, Macromoléculaire et Matériaux, Paris, Francce*

*Corresponding author: arnaud.chaub@espci.psl.eu*

Dynamic gels are 3-dimensional networks in solution that rely on short-lived bonds of functional groups, instead of classical chemical crosslinks. They are widely used as additives to control the rheological properties of solutions, exhibit self-healing properties and can transition from liquid to solid state easily with external stimuli such as temperature.

We have studied hydrophobically-modified alkali-swellable emulsions (HASE), one example of polymeric architecture allowing the formation of dynamic gels. HASE polymer chains are composed of a polyelectrolyte backbone on which are grafted hydrophobic macromonomers that associate intra and inter- chains, acting as physical and reversible crosslinks. HASE solutions are viscoelastic liquids and solids depending on the chemistry of the hydrophobic moieties.

We focus on the rheology of aqueous solutions of a HASE polymer with branched alkyl moieties comprising 32 carbon atoms. We perform a systematic investigation of their rheological properties using small and large amplitude oscillatory shear experiments and startup flow tests. Local deformation profiles are measured using in-situ rheofluorescence particle image velocimetry. At polymer concentrations as low as 0.3 wt%, we find a transition between viscoelastic solutions and dynamic gels with yield stress properties (Figure). The nonlinear response of gels strongly depends on the total polymer concentration and several phenomena are detected and analyzed such as wall slip, shear-banding, and fracture.

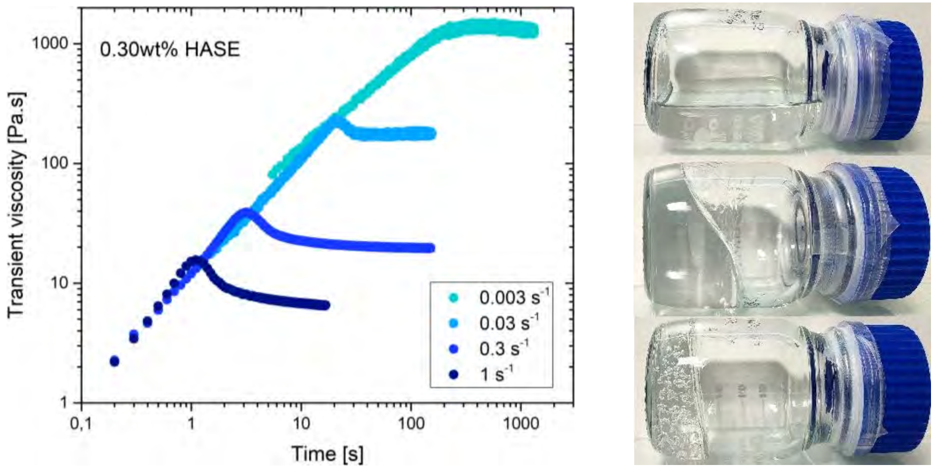


*Figure 1: (left) Transient viscosity versus time at different applied shear rates for 0.30wt% HASE. (right) HASE gels at 0.20wt%, 0.30wt%, 1wt% (from top to bottom).*

# Developing Modelling Tools to Examine Network Formation in Protein Hydrogels

**K. R. Cook** [1], L. Dougan[1], D. Head[2]
[1] *University of Leeds, School of Physics and Astronomy, Leeds, U.K.*
[2] *University of Leeds, School of Computing, Leeds, U.K.*
*Corresponding author: py13kc@leeds.ac.uk*

Folded protein-based hydrogels are ideal materials in biomedicine and biomedical engineering because of their inherent biocompatibility, but little is understood about how their bulk properties extend from the single-molecule level. We develop and employ modelling tools to examine how factors, such as protein volume fraction and cross-linking rate, affect network formation and structure in folded protein hydrogels.

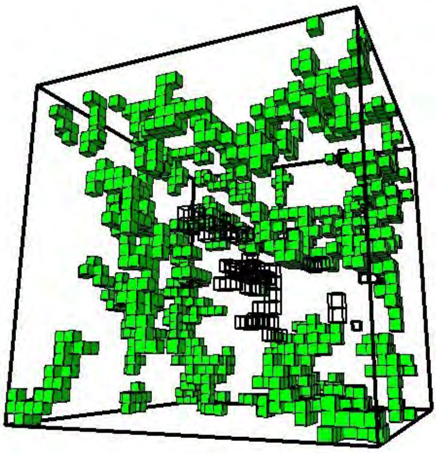


Figure 1: *Gel system at the critical percolation point. Proteins cross-linked in the percolating cluster are represented as green boxes, while non-percolating, intermediate clusters are represented as unfilled boxes.*

We are currently employing a combination of rheology and scattering to study model folded proteins as building blocks in chemically cross-linked hydrogels [1, 2]. Computational modelling offers a powerful way to gain insight into the factors governing protein gelation [3], and using the lattice-based model we have developed, we can efficiently simulate protein clustering and network percolation. Furthermore, we have performed structural analyses on our model gel systems by considering the protein cluster sizes and fractal dimension of the systems at and beyond the precise point of gelation.

## References

[1] M. D. G. Hughes, S. Cussons, N. Mahmoudi, D. J. Brockwell, L. Dougan, *Soft Matter* **2020**, *16*, . DOI:10.1039/c9sm02484k

[2] A. Aufderhorst-Roberts, M. D. G. Hughes, A. Hare, D. A. Head, N. Kapur, D. J. Brockwell, L. Dougan, *Biomacromolecules* **2020**, *21*, 10. DOI:10.1021/acs.biomac.0c01044

[3] B. S. Hanson, L. Dougan *Macromolecules* **2020**, *53*, 17. DOI:10.1021/acs.macromol.0c00890

# Lipid liquid crystalline nanoparticles loaded with manganese oxide nanoparticles (LLCNPs@MnO) – enhancing Magnetic Resonance Imaging contrast agents

**D.K. Flak**[1]; T. Zalewski[1], Ł. Przysiecka[1], K. Fiedorowicz[1], G. Nowaczyk[1]
[1]*Adam Mickiewicz University Poznań, NanoBioMedical Centre, Poznań, Poland*

*Corresponding author: dorfla@amu.edu.pl*

The unique internal structure and morphology of LLCNPs resulting in their higher membrane surface area and hence high loading efficiency, next to their ability to entrap hydrophilic, hydrophobic and amphiphilic molecules, but also their high biocompatibility, makes them potential carriers to be applied in drug and diagnostic agent delivery [1]. In turn, MnO NPs have been recognized as efficient $T_1$ CAs, particularly as ultrasmall NPs and coated/functionalized with biocompatible molecules [2]. Moreover, taking into account the health risks resulting from the use of Gd-chelates and promising effects of using nanoparticles as CAs, Mn-based NPs are seen in the light of recent research as a highly competitive alternative to Gd-based CAs, but also to withdrawn Teslascan®.

In this work we studied a new class of MRI contrast agents (CAs) based on combined hybrid construct consisting of lipid liquid crystalline nanoparticles loaded with MnO nanoparticles (LLCNPs@MnO and LLCNPs@MnO-DMSA). For this purpose two types of MnO nanoparticles were prepared: (1) oleate-capped MnO NPs as hydrophobic ones, and (2) DMSA (meso-2,3-dimercaptosuccinic acid)-functionalized MnO NPs as hydrophilic ones. These MnO NPs were further embedded into LLCNPs, consisting of glyceryl monooleate (GMO) as a structure-forming lipid and Pluronic F-127 as a the non-ionic copolymer surfactant stabilizing LLCNPs in water-based dispersion. The size of as-prepared constructs, varied depending on composition (175.9 nm for unloaded LLCNPs, 246.0 nm for LLCNPs@MnO and 170.6 nm for LLCNPs@MnO-DMSA, PdI was below 0.2). Moreover, these LLCNPs dispersions exhibited good colloidal stability both in water and human plasma-based dispersions (zeta potential was -19.8 mV for unloaded LLCNPs, -20.2 mV for LLCNPs@MnO, and the lowest -16.2mV for LLCNPs@MnO-DMSA). These two hybrid constructs and bare MnO-DMSA were further compared in terms of their biological safety and MRI contrast enhancing ability. Summarizing, obtained hybrid constructs structurally complex (cryo-TEM), were highly biocompatible towards different cells (*in vitro* studies, IC50 ~130 µg/ml) and efficiently internalized into cells. Studied relaxivity ($r_1$) for these constructs at 0.4 T in water and human plasma was significantly improved in comparison to bare MnO-DMSA, even when significantly lower $Mn^{2+}$ ions concentration was used in case of LLCNPs@MnO constructs. Above results achieved for these contrast enhancers give a promise for further efficient *in vivo* imaging.

Acknowledgements
This work was supported by the National Science Center, Poland, under grant SONATA BIS 6 2016/22/E/ST3/00458.

## References

[1] H.M.G Barriga, M.N. Holme, and M.M. Stevens, *Angewandte Chemie International Edition*, **2019**, 58, 2958-2978. DOI: 10.1002/anie.201804067

[2] L. García-Hevia, M. Bañobre-López, and J. Gallo, *Chemistry - A European Journal*, **2019**, 25, 431-441. DOI: 10.1002/chem.201802851

# Co-administration of polyol coated Inorganic Nanoparticles and Antibiotics for enhanced antimicrobial properties.

**K. Giannousi**[1], I. Eleftheriadou[2], C. Dendrinou-Samara[1]

[1]*Aristotle University of Thessaloniki, Laboratory of Inorganic Chemistry, Department of Chemistry, Thessaloniki, 54124, Greece*
[2] *Aristotle University of Thessaloniki, Department of Genetics, Development and Molecular Biology, School of Biology, , 54124, Thessaloniki, Greece*
*Corresponding author: klegia@chem.auth.gr*

The abuse of antimicrobial drugs has led to the upsurge of multidrug-resistant bacteria, representing an extremely serious public health concern. The nanomaterials could be used as innovative tools to combat the ongoing crisis of antimicrobial resistance due to the higher surface to volume ratio enabling high synergy for antimicrobial action. A plethora of inorganic nanoparticles (NPs) has been used as antimicrobial agents. However, their clinical application demands high effective dosages, which induce colloidal dispersion and cytotoxicity problems. Herein, the synthesis of polyol coated CuO, ZnO and bimetallic CuZn NPs is reported.[1,3] The structural and morphological characterization of the NPs was accomplished in the solid and liquid phase. The capped NPs were evaluated in terms of cytotoxicity and antibacterial activity, while their potential role as efflux pump inhibitors has been also investigated against multidrug resistant clinical strains.[2] Drug extrusion by the multidrug efflux pumps represents an important mechanism of multidrug resistance. The co-administration of low dosages of the as-prepared NPs with the antibiotics meropenem and ciprofloxacin towards multi-resistant *Pseudomonas aeruginosa* has led to efflux inhibition and synergistic activity was recorded. The biocompatible-coated NPs are suggested as adjuvant therapy to extend the lifetime of currently used antibiotics, overcoming the costly need for construction of new organic drug formulations and antibiotic scaffolds.

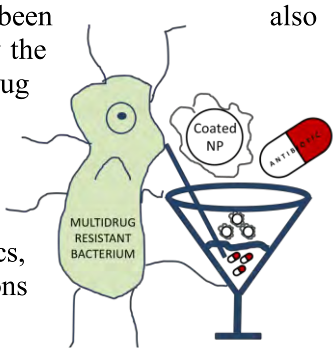


*Figure 1: Cocktail of coated NPs and Antibiotics for addressing multidrug*

## References

1) **K. Giannousi**, G. Geromichalos, D. Kakolyri, S. Mourdikoudis, C. Dendrinou-Samara, Interaction of ZnO nanostructures with proteins: *In vitro* Fibrillation/Antifibrillation studies and in silico molecular docking simulations. *ACS Chem. Neurosci.* **2020**, 11(3), 436-444, https://doi.org/10.1021/acschemneuro.9b00642.
2) **K. Giannousi**, A. Pantazaki, C. Dendrinou-Samara, Copper-Based Nanoparticles as Antimicrobials (Book Chapter) in Nanostructures for Antimicrobial Therapy: Nanostructures in Therapeutic Medicine Series, Pages 515-529, Elsevier, **2017**, 10.1016/B978-0-323-46152-8.00023-8.
3) **K. Giannousi**, E. Hatzivassiliou, S. Mourdikoudis, G. Vourlias, A. Pantazaki and C. Dendrinou-Samara, Synthesis and biological evaluation of PEGylated CuO nanoparticles. *J. Inorg. Biochem.* **2016**, 164:82-90, https://doi.org/10.1016/j.jinorgbio.2016.09.003.

*This research is co-financed by Greece and the European Union (European Social Fund- ESF) through the Operational Programme «Human Resources Development, Education and Lifelong Learning» in the context of the project "Reinforcement of Postdoctoral Researchers - 2nd Cycle" (MIS-5033021), implemented by the State Scholarships Foundation (IKY).*

Ευρωπαϊκή Ένωση
European Social Fund

Operational Programme
Human Resources Development, Education and Lifelong Learning
Co-financed by Greece and the European Union

ΕΣΠΑ
2014-2020
ανάπτυξη - εργασία - αλληλεγγύη

# Stretching Liquid Bridges on Liquid Infused Surfaces

**S. J. Goodband**[1], H. Kusumaatmaja[1], K. Voitchovsky[1]
[1]*Durham University, Department of Physics, Durham, UK*

*Corresponding author: s.j.goodband@durham.ac.uk*

Liquid infused surfaces (LIS) have been shown to exhibit highly desirable anti-fouling properties which can lead to surfaces that are anti-icing, antibacterial, self-healing and anticorrosive. Although their self-cleaning abilities are well known, more work is needed to understand the complex relationship between the oil layer and any attached fouling droplets that form liquid bridges with the surface. While there has been theoretical studies of bridge stretching on LIS surfaces in the quasi-static limit [1], experimental studies, especially those that shed light on the bridge dynamics, are sparse.

In this work, a model LIS system [2] is used to experimentally investigate aqueous capillary bridges formed between two LIS and stretched at different velocities. The force exerted by the bridge and its geometry (contact angle, height and curvature radii) are recorded as a function of the LIS separation. The force profiles can be quantitatively explained with a simple liquid bridge model [3] at low stretching velocities (< 0.01 mm/s). However, significant deviations occur at higher velocities suggesting that mechanisms not captured by the model are at play. Interestingly, the force exerted by the bridge on the LIS decreases with increasing velocity. Additionally, a hysteresis loop opens up over a stretching/recovery cycle indicating previously not considered dissipation mechanisms, possibly in the oil layer [4].

Our experiments provide novel insights into the dynamic behaviour of capillary bridges on LIS and may help inform a functionality-lead development of future LIS. **References**

[1] Alvin C. M. Shek, Ciro Semprebon, Jack R. Panter, and Halim Kusumaatmaja, *Langmuir*, **2021**, 37, 2, DOI: 10.1021/acs.langmuir.0c03220

[2] Sarah J. Goodband, Steven Armstrong, Halim Kusumaatmaja, and Kislon Voïtchovsky, *Langmuir* **2020**, 36, 13, DOI: 10.1021/acs.langmuir.0c00059

[3] Halim Kusumaatmaja and Reinhard Lipowsky, *Langmuir*, **2010**, 26, 24, DOI: 10.1021/la102206d

[4] Armelle Keiser, Ludovic Keiser, Christophe Clanet and David Quéré, *Soft Matter,* **2017**,13, DOI: 10.1039/C7SM01226H

# $CO_2$ incorporation into the head groups of nonionic surfactants – effects on structure and thermodynamics

**M. Gradzielski**[1]; V.J. Spiering[1], R. Marschall[1], A. Ciapetti[1], L. Noirez[2], M.-S. Appavou[3]
[1]*Stranski Laboratorium für Physikalische Chemie, Institut für Chemie, Technische Universität Berlin, Berlin, Germany*
[2]*Laboratoire L8on Brillouin (CEA-CNRS), C.E.-Saclay, 91191 Gif sur Yvette Cedex, France*
[3]*Jülich Centre for Neutron Science (JCNS) at MLZ. 1, 85747 Garching, Germany*

*Corresponding author: e-mail address of corresponding author*

In this work we present an investigation of nonionic surfactants of the $C_iE_j$ type, which were modified by incorporating different amounts of $CO_2$ units into their hydrophilic head groups. This modifies their HLB value and lowers their cmc. Most interestingly the phase behavior of such $CO_2$ modified surfactants differs largely from their conventional analogues by the fact that for high concentration no gel-like liquid crystalline phases are formed [1]. Instead up to the highest concentrations simple Newtonian liquids are present and this behavior was characterized by rheological measurements. This unexpected phase behavior was studied by means of comprehensive static and dynamic light scattering and small-angle neutron scattering experiments (SLS, DLS, SANS). In addition, the thermodynamics of self-assembly were determined from temperature-dependent cmc measurements and more directly from isothermal titration calorimetry (ITC) [2]. These experiments showed that the incorporation of $CO_2$ units imparts a marked hydrophobic character to the surfactants and reduces the repulsive interaction between the aggregates to such an extent that no longer liquid crystalline phases with their unfavorable flow properties are formed. This behavior is highly interesting for the use of nonionic surfactants in formulations at high concentration and can be fully understood based on the aggregate structure and their interactions.

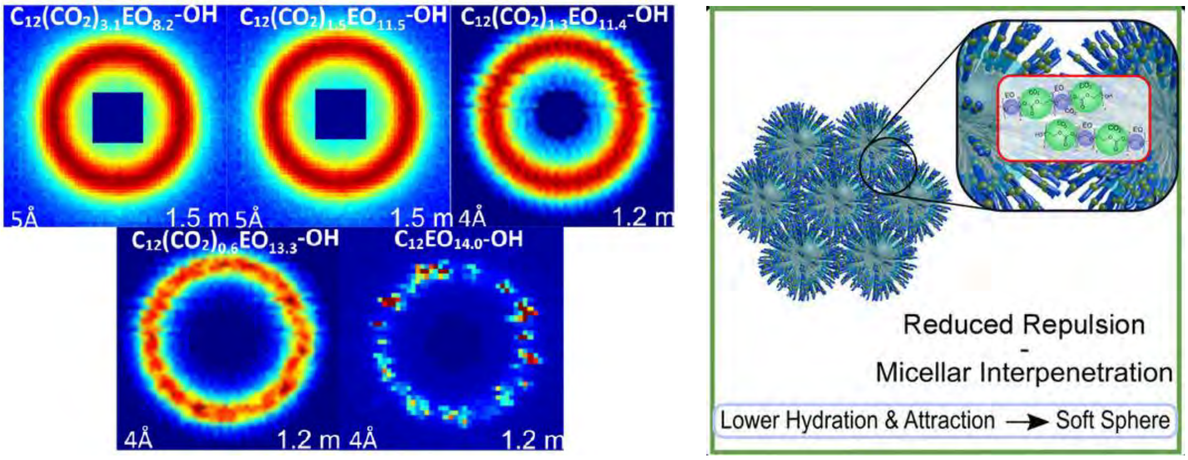


Figure 1: *2D-SANS curves for 50 wt% surfactant samples with different content of $CO_2$ in the head group and scheme of the effect of $CO_2$ incorporation on surfactant aggregation and micellar interactions.*

## References

[1] V. J. Spiering, A. Ciapetti, M. Tupinamba Lima, D. W. Hayward, L. Noirez, M.-S. Appavou, R. Schomäcker, M. Gradzielski, *ChemSusChem* **2020** 13, 601, DOI: 10.1002/cssc.201902855

[2] V. J. Spiering, J. Lutzki, M. Gradzielski, *J. Colloid Interface Sci.* **2021** 581, 794, DOI: 10.1016/j.jcis.2020.07.141

# Quantifying molecular diffusion in thin solvated bio-polymer films

**Saikat Jana**[1]; Rickard Frost[1], Delphine Débarre[2], Ralf P. Richter[1]
[1]*University of Leeds, School of Biomedical Sciences, Faculty of Biological Sciences, School of Physics and Astronomy, Faculty of Engineering and Physical Sciences, Astbury Centre of Structural Molecular Biology, and Bragg Centre for Materials Research, Leeds, United Kingdom*
[2]*Universite Grenoble Alpes, CNRS, LIPhy, 38000 Grenoble, France*

*Corresponding author: S.Jana1@leeds.ac.uk*

Solvated biopolymer coatings are ubiquitous in biomaterials, biosensors, antifouling coatings and separation membranes. These coatings often tens of nanometers thick, occupy much smaller volumes when compared to the illumination volume of a confocal microscope. As a result, while measuring diffusion using microscopy techniques like fluorescence recovery after photobleaching (FRAP) one captures molecular diffusion in bulk solvent rather than in film diffusivity. To overcome this limitation, we confine the polymer films in between a planar and spherical glass surface thereby physically excluding the excess solvent. The resulting plane-sphere contact creates a gap of nanoscale dimensions which allows visualization of molecular diffusion within the solvated films. In addition, by controlling the contact forces one can compress the polymer film to varying amounts within the nanoscale gap. The technique which we call as plane sphere confinement microscopy (PSCM) is used to investigate mechanisms of protein transport through films of end grafted FG Nucleoporins. The FG Nucleoporin films are model systems for studying nuclear pore permeability barrier and allows understanding of mechanisms behind the selective nucleo-cytoplasmic transport of macromolecules in eukaryotic cells. The PSCM technique is employed to gain insights into the in-film diffusivity and partitioning of protein molecules (of different functionalities) as function of compression of the nucleoporin films[1]. We also present the details of a stage insert that implements the PSCM technique and can be installed on fluorescence and/or confocal microscope. The insert is able to engage the plane sphere contact position with sub-micron precision and exerts constant forces in the sub millinewton range, thereby allowing the user flexibility and a greater control over experimental variables. The technique has the potential to enable new investigations in area of functional films and coatings, for example, in understanding the diffusivity of viruses through extracellular matrices or visualizing the assembly of cytoskeletal proteins on cell membranes.

## References

[1] Rickard Frost, Delphine Débarre, Saikat Jana, Fouzia Bano, Jürgen Schüenmann, Dirk Gorlich, Ralf P Richter. *ACS Nano,* **2020** 14(8)**,** 9938-9952, DOI: 10.1021/acsnano.0c02895

# Studies of emulsion droplet distribution in case of hemp seed oil nanoemulsion system

**Maciej Jarzębski**[1]; Wojciech Smułek[2], Farahnaz Fathordoobady[3]; Anubhav Pratap-Singh[3]
[1] *Poznań University of Life Sciences, Department of Physics and Biophysics, Faculty of Food Science and Nutrition, Poznań, Poland*
[2] *Poznan University of Technology, Institute of Chemical Technology and Engineering, Poznań, Poland*
[3] *The University of British Columbia, Faculty of Land and Food Systems, Vancouver, Canada*
*Corresponding author: maciej.jarzebski@up.poznan.pl*

Nanoemulsion systems are one of the most investigated systems due to their possible application for biomedical application and their promising implementation into food technology. Various systems based on oil in water (O/W) and water in oil (W/O) have been studies in case of their stability behavior. Nevertheless, one of the key facto of the emulsion stability is their droplet size. One of the most popular and applied techniques for droplet size distribution is dynamic light scattering (DLS). Here we would like to discuss the way of droplet size distribution in the case of hemp seed oil O/W nanoemulsion systems. Base on our results previous results [1]–[3] we stated that not only z-ave and peak maximum should be discussed in the case of high polydispersity samples. In the presentation, it is recommended to show particle (droplet) size distribution versus scattered light intensity as well as particle number [4]. As a final recommendation, we strongly encourage a minimum of two different techniques for particle size determination or verification homogeneity of the nanoemulsion systems i.e. DLS and microscopic imaging [5].

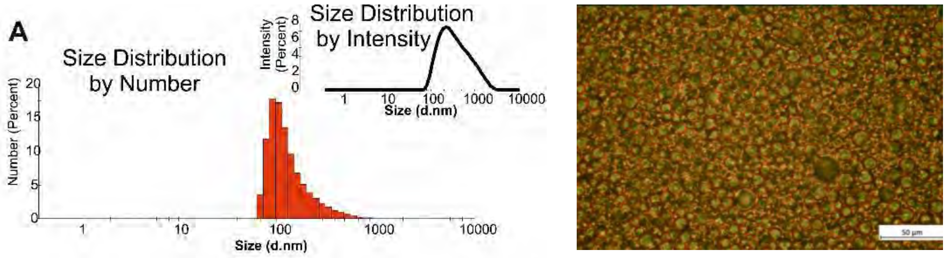


Figure 1: *Nanoemulsion droplet size distribution obtained by DLS and image from the reversed optical microscope (results taken from* [1]*)*

## References

[1] M. Jarzębski *et al.*, “Aesculus hippocastanum L. as a Stabilizer in Hemp Seed Oil Nanoemulsions for Potential Biomedical and Food Applications,” *Int. J. Mol. Sci.*, vol. 22, no. 2, p. 887, Jan. 2021, doi: 10.3390/ijms22020887.
[2] M. Jarzębski *et al.*, “Plant Extracts Containing Saponins Affects the Stability and Biological Activity of Hempseed Oil Emulsion System,” *Molecules*, vol. 25, no. 11, p. 2696, Jun. 2020, doi: 10.3390/molecules25112696.
[3] M. Jarzębski *et al.*, “Pea Protein for Hempseed Oil Nanoemulsion Stabilization,” *Molecules*, vol. 24, no. 23, Nov. 2019, doi: 10.3390/molecules24234288.
[4] M. Jarzębski, P. Siejak, A. Sawerski, M. Stasiak, K. Ratajczak, Ł. Masewicz, A. Pratap-Singh, K. Polewski, F. Fathordoobady, Y. Guo, “Nanoparticles Size Determination by Dynamic Light Scattering in Real (Non-standard) Conditions Regulators - Design, Tests and Applications,” in *Practical Aspects of Chemical Engineering*, M. O. et al. (Eds.), Ed. Springer Nature Switzerland AG 2020, 2020.
[5] M. Jarzębski, B. Bellich, T. Białopiotrowicz, T. Śliwa, J. Kościński, and A. Cesàro, “Particle tracking analysis in food and hydrocolloids investigations,” *Food Hydrocoll.*, vol. 68, pp. 90–101, Jul. 2017, doi: 10.1016/j.foodhyd.2016.09.037.

# Self-diffusion and microstructure of ammonium ionic liquids

**A. Klimaszyk** [1,2], R. Markiewicz[1], M. Jarek[1], S. Jurga[1]
[1]*Adam Mickiewicz University, NanoBioMedical Centre, Poznań, Poland*
[2] *Adam Mickiewicz University, Faculty of Physics, Poznań, Poland*

*Corresponding author: adakli@amu.edu.pl*

Ionic liquids (ILs), organic/inorganic salts with a melting point below 100 $^{o}$C are usually characterized with variety of features, from which common to great group of ILs are low vapor pressure, wide range of liquid state, high thermal, electrochemical and chemical stability, and the ability to dissolve many organic and inorganic compounds, including some polymers. These are properties that conventional solvents do not have, and this is the reason ILs are often considered as green solvents used in laboratory and industrial processes. The specific properties its use, and these depend exclusively on the construction of the anion and cation (changing these two elements, it is possible to design an ionic liquid with the desired physical and chemical properties).

The small differences between ionic liquids (alkyl chain length, type of anion etc.) can have a large effect on their properties. For example, by changing from an ionic liquid with tetrafluoroborate anion, to an ionic liquid with the same cation but a bis(trifluoro-methylsufonyl)imide anion, there is a decrease in the viscosity of the ionic liquid and change from hydrophilic to hydrophobic behaviour, due the nature of the anion.

Physical properties of bulk ILs are affected by different factors, such as chemical structure of the ions, the intra-molecular and inter-molecular interactions, temperature, and the presence of gaseous, liquid or solid impurities.

Diffusion (self-diffusion) coefficient is a parameter, which is not dependent on time and, therefore, can be used to characterise the translational mobility (diffusivity) of a certain type of molecule under certain conditions (temperature, pressure, molecular interactions). As the external conditions change, diffusion coefficient obligatorily also change. For example, an increase in temperature (and, therefore, mean thermal energy of molecules) leads to an increase of D. To describe the temperature dependence of D is not a trivial task. In a simplified assumption it has been described as an activation process of the type of an Arrhenius function.

The aim of this work is the evaluation of microscopic and macroscopic structure of two ammonium ILs' families (with varied cation) solutions as well as the exact characterization of their microscopic interactions by terms of self-diffusion coefficient. In this way, we prepared alkyltriethylammonium and alkylcyclohexyldimethylammonium-based ionic liquids with varied alkyl chain length and bis(trifluoromethylsufonyl)imide anion. After structure confirmation by means of NMR and FTIR, phase transition temperatures were determined by means of differential scanning calorimetry technique. Finally, self-diffusion coefficients were determined for series of the prepared ILs measurements at 14,4 T Agilent NMR spectrometer techniques (DOTY DSI-1372, $g_z$=28 T/m, VnmrJ 4.2; Pulse sequence: PGSE (Pulsed Gradient Spin-Echo).

## References

1. Mecerreyes, D. *Applications of ionic liquids in polymer science and technology*, Springer 2015, ISBN: 3662449021
2. Paluch, M, *Dielectric Properties of Ionic Liquids*, Springer 2016, 978-3-319-32489-0

## Acknowledgments:

A.K. would like to acknowledge the project: "Interdisciplinary PhD studies in nanotechnology " No. POWR.03.02.00-00-I032/16 under the European Social Fund. Moreover, this work was partially funded by the project the H2020-INFRAIA-2016-2017 under research grant "EUSMI – European infrastructure for spectroscopy, scattering and imaging of soft matter", contract number GA731019.

# Transient rheology of model gluten gel in water

Ameur Louhichi[1], Marie-Hélène Morel[2], Laurence Ramos[1] and Amélie Banc[1]

*[1]Laboratoire Charles Coulomb (L2C), Univ.Montpellier, CNRS, Montpellier, France*
*[2]Ingénierie des Agro-Polymères et Technologies Emergentes (IATE), Univ. Montpellier, CIRAD, INRAE, Montpellier, France*

*Corresponding author: amelie.banc@umontpellier.fr*

We investigate the transient viscoelasticity of model gluten gel in water. We used the start-up shear at various rates, from $0.1\ s^{-1}$ to $10\ s^{-1}$, and with different total deformations: 100 SU, 500 SU, 1000 SU and 2000 SU. Thus, transient responses are obtained for the same shear rate window but with changing the mechanical history of samples. The ratio between the maximum and steady stress ($\frac{\sigma_{Max}}{\sigma_{Steady}}$) and strain at the maximum stress ($\gamma_{Max}$) are analyzed for the above experimental conditions.

The transient regime reveals that the gluten gel behaves as a branched polymeric system, with noticeable wakening as a function of the mechanical history.

The ratio $\frac{\sigma_{Max}}{\sigma_{Steady}}$ as a function of shear rate, for the different total deformations, increases with higher total deformation and the data has a shear rate power law dependence that become stronger with total strain, suggesting the weakening of system. Concomitantly, we found that $\gamma_{Max} \geq 10$ for the different experimental conditions, suggesting a strong stretching.

Moreover, the shear rate dependence of both quantities exhibits the presence of two regimes (transition at $\dot{\gamma} \cong 2s^{-1}$ ) only with higher total strains (1000 SU and 2000 SU), suggesting the appearance of new local dynamics in relation with structural changes in the system.

Additional experiments were performed by using supramolecular blockers: urea to disturb hydrogen bonding and N-ethylmaleimide to compete with the thiol/disulfide exchange. The transient data reveals that the effect of supramolecular blockers on the nonlinear transient rheology is comparable to that of the mechanical history, suggesting a common physics driving the mechanical properties of gluten gels under large deformation.

# Temperature-induced structural changes of PNIPAM- from milliseconds to minutes

**J. Michalska**[1]; M. Dulle[1], S. Hauschild[1], S. Förster[1]
[1] *Jülich Centre for Neutron Science (JCNS-1/IBI-8), Forschungszentrum Jülich GmbH, 52425 Jülich, Germany*

*Corresponding author: j.michalska@fz-juelich.de*

Structural changes at the intra- and interchain level induced by the phase transition of poly(N-isopropylacryl amide) (PNIPAM) can be tracked in real-time by time-resolved small-angle neutron scattering (tr-SANS). PNIPAM is one of the most commonly and extensively studied thermoresponsive polymer due to lower critical solution temperature (LCST) in water that occurs at the physiologically relevant temperature. Block copolymer micelles and polymer microgels have been used as drug carriers and as microreactors for enzymatic reactions. For drug release and enzyme reactions, the kinetics of the transport across the micellar core and shell region depends on the local mobility of the core-shell region. The control of time-response is of critical importance for applications of responsive polymers. A general and fundamental understanding of the volume phase transition kinetics is still lacking. The aim of the present study is investigation of the collapse kinetics of PS-PNIPAM micelles by temperature jump above LCST using TR-SANS, light scattering and cryo-electron microscopy. The thermal responsiveness was followed over a broad timescale from the early-stage collapse of polymer in milliseconds to slow growth of aggregates in minutes. Using different experimental methods for homopolymers or micellar block copolymers we got comparable results indicating a common multistep scheme. Thus we concluded a general mechanism for PNIPAM polymers behavior depending on the temperature.

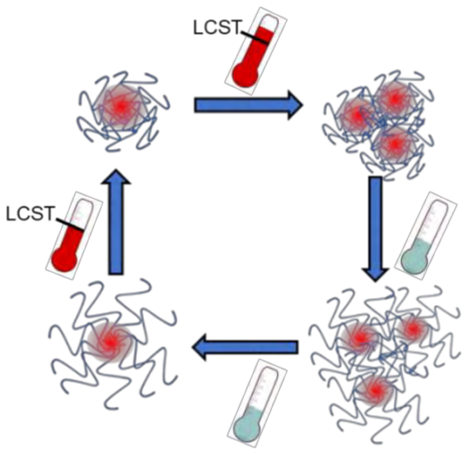


Figure 1: *Temperature-dependence of the multistep behavior of polymer in water.*

# Changing the flow profile and resulting drying pattern of dispersion droplets via contact angle modification

Carmen Morcillo Perez[1], Marcel Rey[1], Benjamin D. Goddard[2], and Job H. J. Thijssen[1]

[1]*The University of Edinburgh, SUPA School of Physics and Astronomy, Edinburgh, United Kingdom*
[2]*The University of Edinburgh, School of Mathematics, Edinburgh, United Kingdom*

*Corresponding author: carmen.morcillo.perez@ed.ac.uk*

Prediction and control over particle deposit patterns obtained from sessile droplet evaporation are essential for many industrial processes, such as inkjet printing and crop protection. Numerous formulations have been studied in order to understand how the different components affect the final dried deposit. Yet, the testing substrates used are generally far from similar to those in the real application. Thus, a key challenge resides in understanding how the substrate properties can affect the drying process. We present a systematic investigation on the effect of surface wettability on the evaporation dynamics of a particle-laden droplet and the final distribution of the particles after evaporation. We tuned the wettability of glass slides using silanisation reactions; and measured the flow inside the drying droplets using fluorescent tracer particles and particle tracking algorithms. We found that the internal flows shift from predominantly outwards flow for low contact angles to predominantly inward flow for large contact angles. Upon increasing the substrates hydrophobicity, the dried deposit gradually changes from the typical coffee-ring to a central stain, as the evaporation is no longer fastest at the contact line. On the basis of the results obtained, we conclude that the substrate plays an essential role on the drying process and supports the need for improved procedures during formulation design.

# Rheological and structural properties of polyacrylamide microgels designed by two different synthesis strategies

A. Mungroo[1]
*IMP Laboratory, Jean Monnet University of Saint-Etienne, France*

*Corresponding author: ashley.mungroo@univ-st-etienne.fr*

Unveiled by Baker[1] in 1949 microgels are remarkable materials describing a colloidal dispersion of cross-linked polymers micro-network with the ability to swell in good solvent. Nowadays, we are able to tailor-made their ability to swell depending on the stimuli applied such as the temperature, pH or ionic strength. In this work, we focused our attention on crosslinked polyacrylamide microgels which have attracted a lot of attention this past decade thanks to their water solubility, extremely valuable for bioapplications as biosensors[2], [3] and for oil recovery applications[4]. We compared two different types of synthesis procedures: inverse microemulsion polymerization (IMEP) and precipitation polymerization (PP) using light scattering and rheological measurements. We investigated the influence of solvent and crosslinking on microgels architecture and on their rheological properties. We shed lights on the use of a co- solvent in PP which allowed to control the hydrodynamic radius ($R_H$) of PAAm microgels and the reduction of the amount of crosslinker drastically decreased the turbidity of the PAAm microgels aqueous solution. We compared the shear rheological responses pointing out that PAAm microgels prepared via PP are soften (and so have lesser density of crosslinking) than those prepared via IMEP.

## References

[1] W. O. Baker, "Microgel, A New Macromolecule," *Ind. Eng. Chem.*, vol. 41, no. 3, pp. 511–520, 1949, doi: 10.1021/ie50471a016.

[2] M. I. González-Sánchez, J. Rubio-Retama, E. López-Cabarcos, and E. Valero, "Development of an acetaminophen amperometric biosensor based on peroxidase entrapped in polyacrylamide microgels," *Biosens. Bioelectron.*, vol. 26, no. 5, pp. 1883–1889, 2011, doi: 10.1016/j.bios.2010.03.024.

[3] J. P. Hervás Pérez, M. Sánchez-Paniagua López, E. López-Cabarcos, and B. López-Ruiz, "Amperometric tyrosinase biosensor based on polyacrylamide microgels," *Biosens. Bioelectron.*, vol. 22, no. 3, pp. 429–439, 2006, doi: 10.1016/j.bios.2006.05.015.

[4] Z. Chen, "Polyacrylamide and its derivatives for oil recovery," *Missouri Univ. Sci. Technol.*, p. 2532, 2016.

# Revealing the origin of the specificity of calcium and sodium cations binding to adsorption monolayers of two anionic surfactants

**F. Mustan**,[1] A. Ivanova,[2] S. Tcholakova,[1] N. Denkov[2]
[1] *University of Sofia, Department of Chemical and Pharmaceutical Engineering, Sofia, Bulgaria*
[2] *University of Sofia, Department of Physical Chemistry, Sofia, Bulgaria*

*Corresponding author: fm@lcpe.uni-sofia.bg*

The studied anionic surfactants linear alkyl benzene sulfonate (LAS) and sodium lauryl ether sulfate (SLES) are widely used key ingredients in many home and personal care products. These two surfactants are known to react very differently with multivalent counter-ions, including $Ca^{2+}$. This is explained by a stronger interaction of the calcium cation with the LAS molecules, when compared to SLES. The molecular origin of this difference in the interactions remains unclear. In the current study, we conduct classical atomistic molecular dynamics simulations to compare the ion interactions with the adsorption layers of these two surfactants, formed at the vacuum-water interface. Trajectories of 150 ns are generated to characterize the adsorption layer structure and the binding of $Na^+$ and $Ca^{2+}$ ions. We found that both surfactants behave similarly in the presence of $Na^+$ ions. However, when $Ca^{2+}$ is added, $Na^+$ ions are completely displaced from the surface with adsorbed LAS molecules, while this displacement occurs only partially for SLES. The simulations show that the preference of $Ca^{2+}$ to the LAS molecules is due to a strong specific attraction with the sulfonate head-group, beside the electrostatic one. This specific attraction involves significant reduction of the hydration shells of the interacting calcium cation and sulfonate group, which couple directly and form surface clusters of LAS molecules, coordinated around adsorbed $Ca^{2+}$ ions. In contrast, SLES molecules do not exhibit such specific interaction, because the hydration shell around the sulfate anion is more stable, due to the extra oxygen atom in the sulfate group, thus precluding substantial dehydration and direct coupling with any of the cations studied.

# Multiresponsive starPEG-hydrogels crosslinked with pyrene-functionalized copolymers

**Dustin Rasch**[1,2], Robert Göstl[1]
[1]*DWI – Leibniz-Institute for Interactive Materials, Aachen, Germany*
[2]*Institute of Technical and Macromolecular Chemistry, RWTH Aachen University, Aachen, Germany*

*Corresponding author: goestl@dwi.rwth-aachen.de*

Pyrene is widely used as fluorescent, distance-sensitive sensor powered by its excimer formation and emission. Yet, distance sensing based on pyrene relies on the interplay of multiple intricate spectroscopic phenomena. Especially in aqueous solution, the hydrophobic character of pyrene leads to the interference of different effects rendering the reproducible collection and meaningful analysis of the obtained spectral data non-trivial.

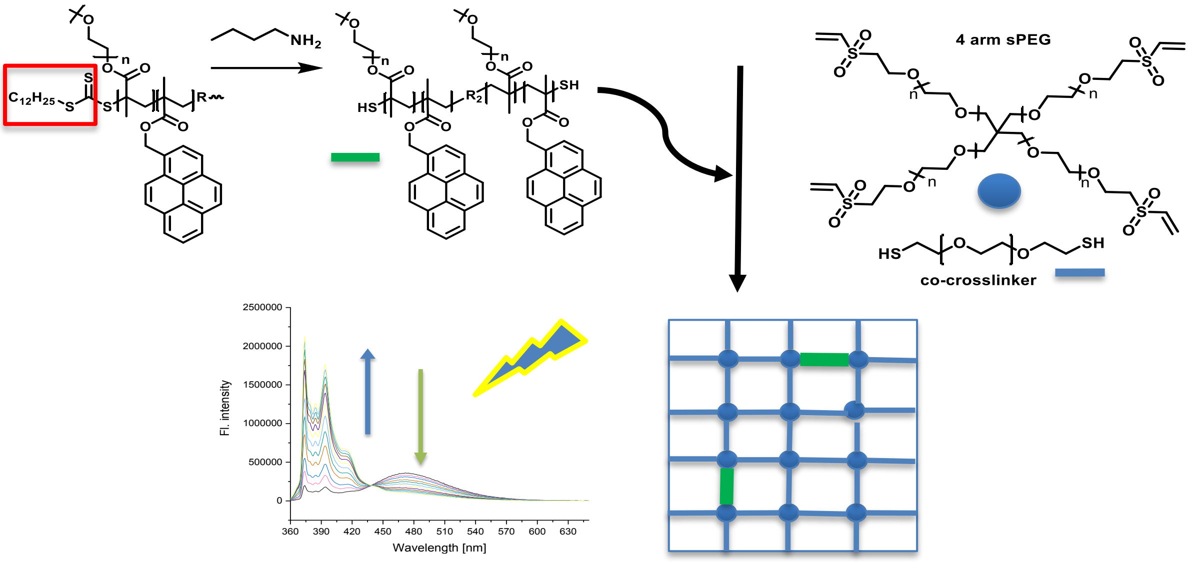


Figure 1: *Synthesis strategy for multiresponsive starPEG hydrogels and photoinduced pyrene cleavage from the macromolecules.*

We investigated a series of well-defined statistical copolymers composed of pyrenylmethyl methacrylate (PyMA) and oligo(ethylene glycol) methyl ether methacrylate (OEGMEMA) with varying pyrene content (Figure 1). By chemical modification of the end-groups, these were incorporated as covalent macrocrosslinkers into starPEG hydrogels. The emissive properties of the obtained materials was strongly dominated by intra- and intermolecular effects depending on the pyrene concentration within each chain and the overall macrocrosslinker concentration. We show that static excimer formation, which we clearly distinguish from dynamic pyrene excimer emission, is a major contributor to these observed effects.

The resulting hydrogels were shown to be multi-responsive and photoinduced pyrene cleavage was used for irreversible photolithography in these materials. In addition, the controlled swelling of the hydrogels with discrete amounts of water revealed a novel counterintuitive chromatic effect, which was used to control the lithographic process.

# Innovative microfluidic platforms for biomedical applications. Novel technologies for the obtaining of functionalized bioceramics and hybrid hydrogel microparticles production.

**Ramón Rial**[1*]; Juan M. Ruso[1]

[1]*University of Santiago de Compostela, Soft Matter and Molecular Biophysics Group, Department of Applied Physics, Santiago de Compostela, Spain*

**Corresponding author: ramon.rial@usc.es*

This work focuses on the production of new sophisticated biomaterials for their use in modern tissue regeneration approaches. New strategies [1, 2] and novel synthetic routes [3] were successfully developed. The resultant biomaterials are economically feasible and their refined attributes help them becoming a great solution in numerous applications in tissue regeneration and biomedical engineering.

Particularly, bioceramic nanoparticles attract a lot of attention within the biomedical device industry. Nevertheless, most of their potential uses are conditioned by their shapes and morphologies, so controlling their synthesis is a more than efficient way of enhancing their properties. In this regard, microfluidic techniques are a highly helpful tool which allows a great precision on the management of flows and concentrations. In particular, one of the innovations of this work is the conception and the effective development of a new procedure for the obtaining of hydroxyapatite nanorods (HAp). This novel methodology, apart from notably reducing the production costs, also enables the manipulation of the synthesis conditions, allowing to fine tune the structure of the resulting nanorods by simple engineering, just varying inlet flow velocities and ratios.

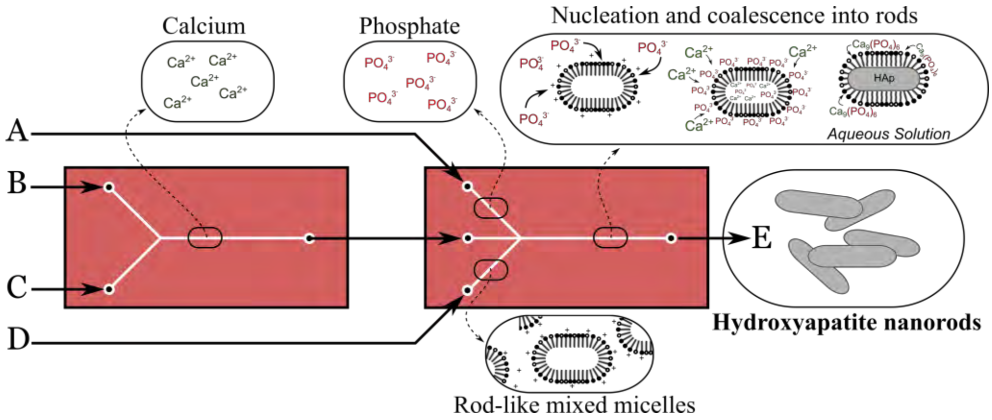


Figure 1: Schematic representation of the microfluidic system operation.

Similarly, a new method for the synthesis of crosslinked hydrogel microparticles (HMPs) was also developed. Typically, hydrogels are made as solid materials with macroscale external dimensions and nanoscale internal mesh sizes. However, for certain uses, such as injection or extruded-based 3D printing, bulk hydrogels have inherent drawbacks[4]. To address this problem, hydrogel microparticles (HMPs) are emerging as a promising solution in this field, due to their modular nature, the adjustability of the level of porosity and their ability to flow through small needles or catheters[5][6]. This work describes the procedure for obtaining hydrogel microspheres for doped-hydroxyapatite encapsulation and controlled drug delivery. Combining external and internal gelation, it is possible to obtain Calcium-Alginate microparticles (Ca-ALG) and core-shell Calcium-Alginate-Chitosan microspheres (Ca-ALG-CHI) with homogeneous sizes and morphologies and load them with doped HA. The study of this kind of micro-hydrogels with advanced functionalities is crucial for the construction of granular hydrogels, which are a very promising solution for a great array of modern therapies in regenerative medicine areas.

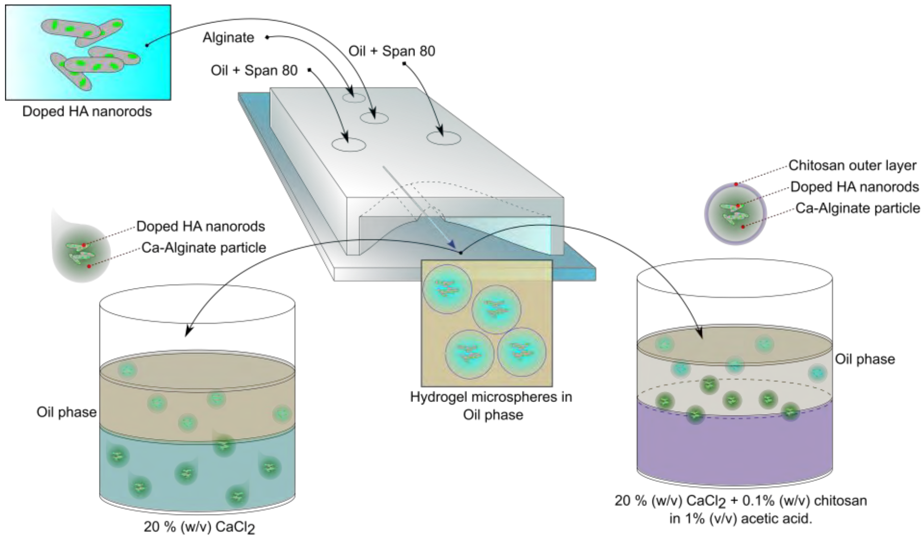


Figure 2: Microfluidic set-up for the hybrid hydrogel microparticles production. Spherical droplets are created inside the microchanels of the chip. After the collection in the gelation baths, two different microparticles are obtained: teardrop-shaped Ca-Alg microparticles and spherical core-shell ALG-CHI microgels.

## References

[1] R. Rial, Z. Liu, and J. M. Ruso, "Soft Actuated Hybrid Hydrogel with Bioinspired Complexity to Control Mechanical Flexure Behavior for Tissue Engineering," *Nanomaterials,* vol. 10, p. 1302, 2020.

[2] N. L. D'Elía, R. Rial Silva, J. Sartuqui, D. Ercoli, J. Ruso, P. Messina*, et al.*, "Development and characterisation of bilayered periosteum-inspired composite membranes based on sodium alginate-hydroxyapatite nanoparticles," *Journal of Colloid and Interface Science,* vol. 572, pp. 408-420, 2020/07/15/ 2020.

[3] R. Rial, P. G. Tahoces, N. Hassan, M. L. Cordero, Z. Liu, and J. M. Ruso, "Noble microfluidic system for bioceramic nanoparticles engineering," *Materials Science and Engineering: C,* vol. 102, pp. 221-227, 2019/09/01/ 2019.

[4] A. C. Daly, L. Riley, T. Segura, and J. A. Burdick, "Hydrogel microparticles for biomedical applications," *Nature Reviews Materials,* vol. 5, pp. 20-43, 2020/01/01 2020.

[5] J. E. Mealy, J. J. Chung, H.-H. Jeong, D. Issadore, D. Lee, P. Atluri*, et al.*, "Injectable Granular Hydrogels with Multifunctional Properties for Biomedical Applications," *Advanced Materials,* vol. 30, p. 1705912, 2018.

[6] E. Sideris, D. R. Griffin, Y. Ding, S. Li, W. M. Weaver, D. Di Carlo*, et al.*, "Particle Hydrogels Based on Hyaluronic Acid Building Blocks," *ACS Biomaterials Science & Engineering,* vol. 2, pp. 2034-2041, 2016/11/14 2016.

# On the effect of particle morphology and interaction on near wall dynamics

**J. A. Rivera Morán** [1], Y. Liu[1], S. Monter[1,2], M. Lisicki[3], C.-P. Hsu[4], P, R. Lang[1]
[1] *Forschungszentrum Jülich GmbH, IBI-4, Jülich, Germany*
[2] *Universität Konstanz, Germany*
[3] *University of Warsaw, Physics Department, Warsaw, Poland*
[4] *Eidgenössische Technische Hochschule , Department of Materials, Zürich, Switzerland*
*Corresponding author: j.rivera.moran@fz-juelich.de, p.lang@fz-juelich.de*

We employed evanescent wave dynamic light scattering[1] to study the near wall dynamics of different types of silica particles, i. e. full spheres, spherical shells and spheres with surface roughness, with the objective to investigate the effect of particle morphology on their near wall dynamics.

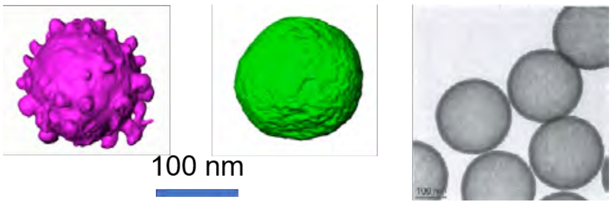


Figure 1: *Investigated particle types: 3D-reconstructions of a rough (left) and of a smooth (middle) silica particle from cryo-TEM. TEM-image of silica-shells (right)*

While the dynamics of spherical particles and hollow shells is in agreement with theoretical predictions for hard sphere colloids[2] within experimental error, the rough particles show slower dynamics than expected for spheres. As the latter finding is at conflict with hydrodynamic theory, we further investigated the influence of static particle wall interaction on the dynamics. Our results indicate that the rough particles experience stronger van der Waals attraction than particles with a smooth surface, which may contribute to settle an open question in literature concerning the effect of particle roughens on interaction and adhesion[3, 4].

## References

[1] P. Holmqvist, J. K. G. Dhont, P. R. Lang, *J. Chem. Phys.* **2007**, *126*, 044707 1-8. DOI:10.1063/1.2431175.

[2] A. J. Goldman, R. G. Cox and H. Brenner *Chem. Eng. Sci.* **1967**, *22*, 637. DOI:10.1016/0009-2509(67)80047-2

[3] S. Bhattacharjee, C. H. Ko, M Elimelech, *Langmuir* **1998**, *14*, 3365. DOI:10.1021/la971360b.

[4] J. Y. Walz and N. Sun *Particles on Surfaces* **2002**, *7*, 151.

# Role of the environment in tuning the dynamical transition of PNIPAM: a neutron scattering study

**B. P. Rosi** [1], A. D'Angelo[2], M. Zanatta[3], A. Paciaroni[1], S. Corezzi[1], L. Comez[4], C. Petrillo[1], F. Sacchetti[1], A. Orecchini[1,4]
[1] *Università di Perugia, Dipartimento di Fisica e Geologia, Perugia, Italy*
[2] *CNRS c/o Université Paris-Saclay, Laboratoire de Physique des Solides, Paris, France*
[3] *Università di Trento, Dipartimento di Fisica, Trento, Italy*
[4] *CNR-IOM c/o Università di Perugia, Dipartimento di Fisica e Geologia, Perugia, Italy*
*Corresponding author:benedettapetra.rosi@unipg.it*

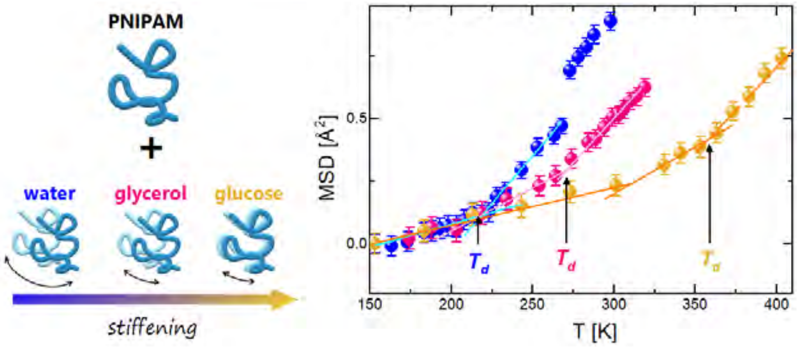


Figure 1: *Mean square displacements (MSD) of PNIPAM samples in the presence of different environments. The MSD are obtained by the EINS intensities collected at the IN13 neutron spectrometer that samples motions on a time scale of about 150 ps. Black arrows indicate the dynamical transition temperature $T_d$ for each sample.*

Hydrated proteins undergo a dynamical transition (DT) at $T_d \approx 200$ K that is associated with the activation of protein dynamics on the ps to ns time scales, that are made accessible by Elastic Incoherent Neutron Scattering (EINS) experiments. The transition is accompanied with an increased flexibility that is ascribed to a plasticizing action exerted by water, thanks to the tight coupling between protein and solvent. This aspect has attracted the widest interest, since flexibility is deemed as necessary to perform biological functions. The impact of the environment on protein flexibility and dynamics has been further explored by substituting water with *stabilizing* compounds usually employed for storage of proteins, in order to preserve them from degradation. Several studies have shown that stabilizers stiffen protein motions and shift $T_d$ toward higher values, suggesting a connection between preservative action and inhibition of fast dynamics. Quite surprisingly, a DT has also been recently observed in a hydrated synthetic polymer, i.e. poly($N$-isopropylacrylamide) or PNIPAM [1], making it an excellent case study for investigating the connection between solvent characteristics, macromolecular flexibility and activation of the DT. By means of EINS techniques we studied the impact of stabilizers on the fast dynamics of PNIPAM, revealing strong analogies with protein behaviour.

## References

[1] Tavagnacco *et al.*, *Phys. Rev. Res.* **2021**, *3*, 013191. DOI:10.1103/PhysRevResearch.3.013191. Tavagnacco *et al.*, *J. Phys. Chem. Lett.* **2019**, *10*, 870–876. DOI:10.1021/acs.jpclett.9b00190. Zanatta *et al. Sci. Adv.* **2018**, *4*, eeat5895. DOI:10.1126/sciadv.aat5895.

# TRACKING COLLOIDAL PARTICLES TO EVALUATE THEIR DISPERSION UNDER SHEAR APPLICATIONS

**M. Saeed[1]; A. Otsuki[1,2].**
[1]*University of Lorraine, ENSG, GeoRessources, Vandoeuvre-les-Nancy, France*
[2]*Luleå University of Technology, Waste Science Technology, Luleå, Sweden*

*Corresponding author: akira.otsuki@univ-lorraine.fr*

We studied the effect of shear rate (0-500 $s^{-1}$) and solution pH (6, 10) on the dispersion degree of colloidal silica particles via the determination and comparison of interparticle distances. Silica particle suspensions prepared at desired pH and solid concentrations were monitored using a confocal rhescope with the shear rates from 0 to 500 $s^{-1}$ and then decreased back to 0 $s^{-1}$. Images corresponding different shear rates (0, 0.005, 0.05, 0.5, 5, 50, 500 $s^{-1}$) were treated with Fiji / image J software and coordinates of the particles were identified. These coordinates were then treated in Visual studio to calculate the distance among the particles. It was found that population of the particles under different shear rates varied and less number of particles per unit area of the image were identified with the increasing shear rate.

# One-Component DNA Mechanoprobes for Facile Mechanosensing in Photopolymerized Hydrogels and Elastomers

**R.S. Schmidt**[1]; G. Creusen[1], A. Walther[1,2*]
[1]*A³BMS Lab, Department of Chemistry, University of Mainz, 55128 Mainz, Germany*
[2]*DFG Cluster of Excellence "Living, Adaptive and Energy-Autonomous Materials Systems"* *(liv*MatS*), 79110 Freiburg, Germany*

**Corresponding author: andreas.walther@uni-mainz.de*

The combination of mechanical sensory functions with easily detectable visual output is a key feature towards fundamental understanding of e.g. cell behavior and the design of responsive materials systems e.g. in tissue engineering. The translation of a mechanical force into an optical readout is accessible via DNA nanotechnology, providing a toolbox living up to multiple requests in today's materials systems. The programmability of DNA-based motifs enables bond directionality, control over the force range, and orthogonality in the use of multiple force sensors.

We herein describe the development of a new approach towards an all-in-one DNA-based fluorescent mechanosensing macro-monomer easily implementable into hydrogel networks by free radical polymerization (**Figure 1**). In contrast to previous designs of DNA mechanoprobes that contain multiple individual strands, we herein merge all relevant components synthetically into a single and highly robust entity. The mechanosensing feature relies on hybridization of single stranded DNA (ssDNA) folding into a hairpin loop, immobilizing the fluorophore-quencher pair (added as in strand modifications) for the optical force sensor readout at the root of the motif. Both termini of the mechanoprobe are modified with methacrylamide functionalities, assuring simple incorporation into the polymer network of hydrogels by free radical polymerization. We demonstrate mechanoactivation in hydrogels and in solvent-free elastomers.

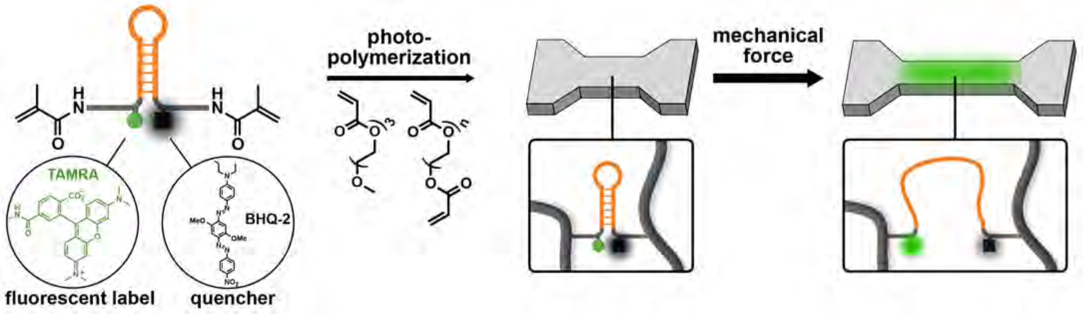


Figure 1: *All-in-one DNA mechanoprobes and their incorporation into the hydrogel network via photopolymerization. Mechanical stress is visualized by the DNA force sensor via an increase in fluorescence upon spatial separation of the dye-quencher pair.*

Our simplified all-in-one design overcomes two major bottlenecks currently limiting wider application of DNA-based mechanofluorescent probes in (bio)materials research: (1) reliable correct folding of the mechanoprobe by a single-component hairpin design with internal dye-quencher modifications for the optical readout without the requirement of a complex annealing protocol including multiple components, and (2) reliable implementation of the force sensing motif by direct incorporation of the DNA mechanoprobe into the polymer network of the hydrogel via free radical polymerization without requiring further DNA interfaces.

# Building blocks of protein structures

**T. Škrbić** [1,2], J. R. Banavar[1], A. Giacometti[2], T. X. Hoang[3],A. Maritan[4],G. Rose[5]
[1] *University of Oregon, Department of Physics and Institute for Fundamental Science, Eugene, Oregon, USA*
[2] *Università Ca Foscari, Dipartimento di Scienze Molecolari e Nanosistemi, Venezia, Italy*
[3] *Vietnam Academy of Science and Technology, Institute of Physics, Hanoi, Vietnam*
[4] *Università di Padova, Dipartimento di Fisica e Astronomia, Padova, Italy*
[5] *Johns Hopkins University, T. C. Jenkins Department of Biophysics, Baltimore, Maryland, USA*
*Corresponding author:tskrbic@uoregon.edu*

We present a prediction of the building blocks of protein structures with no chemistry and no adjustable parameters. Our predictions arise from one hypothesis that the dominant folding mechanism of a protein is the drive to maximize its self-interaction, thereby attaining a space-filling folded state. Our results are in good accord with experimental data on more than four thousand protein structures and they underscore the consilience in the fit of chemistry and biology to the dictates of mathematics and physics. Our work has consequences for the energy landscape of proteins and the role of evolution in shaping sequences and functionalities.

## References

[1] T. Škrbić, A. Maritan, A. Giacometti, G. D. Rose and J. R. Banavar, *Phys. Rev. E* (2021), in press

[2] T. Škrbić, A. Maritan, A. Giacometti, G. D. Rose and J. R. Banavar, bioRxiv (2021), https://doi.org/10.1101/2020.11.10.375105

# Structure of dense adsorption layers of escin at the air-water interface studied by molecular dynamics simulations

**S. Tsibranska**[1]; A. Ivanova[2], S. Tcholakova[1], N. Denkov[1]
[1]*Faculty of Chemistry and Pharmacy, University of Sofia, Department of Chemical and Pharmaceutical Engineering, Sofia, Bulgaria*
[2]*Faculty of Chemistry and Pharmacy, University of Sofia, Department of Physical Chemistry, Sofia, Bulgaria*

*Corresponding author: st@lcpe.uni-sofia.bg*

Saponins are abundant natural surfactants applied in pharmaceutical, food and beverage industries, due to their strong surface activity. Saponins have also various types of useful bioactivity. One of the saponins with very interesting properties is escin, extracted from horse chestnut. The escin adsorption layers, formed at the air-water interface, have unusually high surface visco-elasticity and relatively low permittivity to gas molecules [1,2]. In a previous study [3], using molecular dynamics simulations, we investigated the molecular origin of this behavior with diluted adsorption layers. We found that the escin molecules rapidly self-assemble in clusters on the air-water interface, due to the combined action of several attractive interactions [3]. Here we present a continuation of our previous study with atomistic molecular simulations of dense escin adsorption layers. The major aim is to obtain deeper insight into the alignment and the interactions between the escin molecules in such dense layers. The molecular orientation at the interface is determined in two models, with different areas per escin molecule in the adsorption layer. The results show that the high flexibility of the hydrophilic sugar groups in the escin molecule, combined with the attractive molecular interactions, lead to fast molecular rearrangement into densely packed adsorption layers. The layer thickness and the surface tension calculated from the computer simulations agree with the experimental data [1,2], thus confirming the reliability of the model used. The new simulations confirm our previous conclusion [3] that a specific interaction, which appears as an intermediate between the classical short-range hydrogen bonding and the conventional dipole-dipole attraction, is the key to explain the substantial surface visco-elasticity of the escin adsorption layers.

## References

[1] N. Pagureva, S. Tcholakova, K. Golemanov, N. Denkov, E. Pelan, S. Stoyanov *Colloids Surfaces A,* **2016** 491**,** 18, DOI: 10.1016/j.colsurfa.2015.12.001

[2] J. Penfold, R. K. Thomas, I. Tucker, J. T. Petkov, S. D. Stoyanov, N. Denkov, K. Golemanov, S. Tcholakova, J. R. P. Webster *Langmuir,* **2018** 34**,** 9540, DOI: 10.1021/acs.langmuir.8b02158

[3] S. Tsibranska, A. Ivanova, S. Tcholakova, N. Denkov *Langmuir,* **2017** 33**,** 8330, DOI: 10.1021/acs.langmuir.7b01719