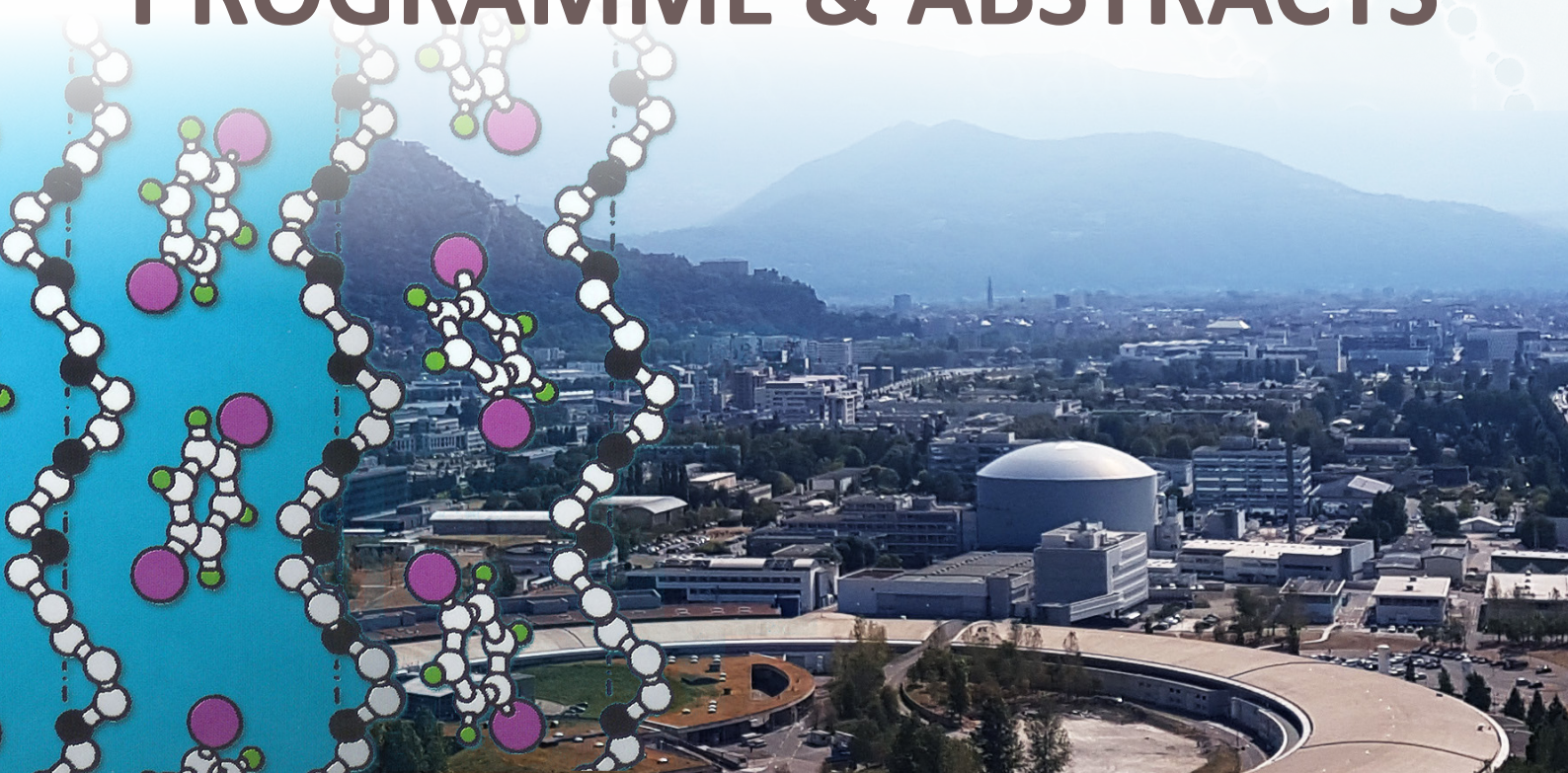


POLYSOLVAT-12

12th International IUPAC Conference
on Polymer-Solvent Complexes and Intercalates

PROGRAMME & ABSTRACTS



4-7 September, 2018

Institut Laue-Langevin, Grenoble, France



I U P A C

INTERNATIONAL UNION OF
PURE AND APPLIED CHEMISTRY



**12th International IUPAC Conference on
Polymer-Solvent Complexes and Intercalates**

POLYSOLVAT-12

Organized by

Institut Laue-Langevin

71 Avenue des Martyrs, 38000 Grenoble, France

and

Centre de Recherches sur les Macromolécules Végétales - CNRS

601 Rue de la Chimie, Domaine Universitaire, 38400 Saint-Martin-d'Hères

e-mail: polysolvat12@ill.eu

website: <https://workshops.ill.fr/e/polysolvat12>



Presentation and scope

Polysolvat-12 is the new edition in a series of successful international meetings organized every two years. The conference focuses on the formation mechanisms, the morphology, the molecular structure, and the properties of compounds from synthetic polymers, biopolymers, proteins, and supramolecular polymers. Bulk state, solutions and systems formed at surfaces/interfaces are considered.

The previous five meetings took place at:

2016 - Kolkata, India
2014 - Salerno, Italy
2012 - Kiev, Ukraine
2010 - Strasbourg, France
2008 - Marrakech, Morocco

Articles based upon conference communications have been published in dedicated volumes of *Macromolecular Symposia*, as will also be the case for Polysolvat-12.

Organization

International scientific committee:

Laure BINIEK, Institut Charles Sadron, CNRS, Strasbourg (France)
Angiolina COMOTTI, University of Milan Bicocca, Milan (Italy)
Christophe DANIEL, Università degli Studi di Salerno, Salerno (Italy)
Said EL HASRI, Cadi Ayyad University, Marrakech (Morocco)
Bhoje E. GOWD, CSIR - National Institute for Interdisciplinary Science and Technology (India)
Yves GROHENS, Université de Bretagne-Sud, Lorient (France)
Jean-Michel GUENET, Institut Charles Sadron, CNRS, Strasbourg (France)
Rebeca HERNANDEZ, Institute of Polymer Science and Technology, CSIC, Madrid (Spain)
Michael HESS, IUPAC Polymer Division - University of North Texas, Denton (USA)
Hideyuki ITAGAKI, Shizuoka University, Shizuoka (Japan)
Natalya KUTSEVOL, Taras Shevchenko University, Kiev (Ukraine)
Sudip MALIK, Indian Association for the Cultivation of Science (IACS), Kolkata (India)
Aline MILLER, Manchester University, Manchester (UK)
Pellegrino MUSTO, Institute of Polymers Composites and Biomaterials, Pozzuoli (Italy)
Arun Kumar NANDI, Indian Association for the Cultivation of Science, Kolkata (India)
Jean-Luc PUTAUX, CERMAV-CNRS, Grenoble (France)
Jiri SPEVACEK, Institute of Macromolecular Chemistry, Prague (Czech Republic)

Local organization committee:

Chairman: **Jean-Luc PUTAUX** (CERMAV)

Co-chairman: **Trevor FORSYTH** (ILL)

Members: **Sylvain PREVOST**, **Ralf SCHWEINS**, **Alison MADER** (ILL), **Yu OGAWA** (CERMAV)
with help from **Sandrine COINDET** and **Céline LARTIGUE** (CERMAV) and **Serge CLAISSE** (ILL)

Programme overview

Tuesday – 4 September		Wednesday – 5 September	
		09:00-09:40	Anna Mitraki
		9:40-10:00	Ryo Mizuta
		10:00-10:20	Trevor Forsyth
		10:20-10:50	Coffee break - Hall ILL 4
		10:50-11:30	Martin Weik
11:30-12:30	Early Registration (mandatory for people eating at the canteen)	11:30-11:50	Giovanna Fragneto
12:00-13:30	Lunch - self-service at ILL/ESRF canteen	11:50-12:10	Florent Bernaudat
13:30-14:00	Registration	12:10-14:00	Lunch - self-service at ILL/ESRF canteen
14:00-14:30	Welcome address	14:00-14:40	Marie Plazanet
14:30-15:10	Jean-Michel Guenet	14:40-15:00	Fumitoshi Kaneko
15:10-15:30	Christophe Daniel	15:00-15:20	Nicolas Le Moigne
15:30-15:50	Cong-Anh-Khanh Le	15:20-15:50	Coffee break - Hall ILL 4
15:50-16:20	Coffee break - Hall ILL 4	15:50-16:30	Rebeca Hernández
16:20-17:00	Petr Stepanek	16:30-16:50	Sujoy Das
17:00-17:20	Esther Cazares Cortes	16:50-17:10	Lamia Bedjaoui-Alachaher
17:20-17:40	<i>to be announced</i>	17:30-20:00	Poster session
			Wine & cheese
	Free evening		
Thursday – 6 September		Friday - 7 September	
9:00-9:40	Olli Ikkala	09:00-9:40	Rachel Auzély
9:40-10:00	Yoshiharu Nishiyama	9:40-10:00	Isabelle Grillo
10:00-10:20	Sonia M. Aguilera-Segura	10:00-10:20	Akkacha Mazari
10:20-10:50	Coffee break - Hall ILL 4	10:20-10:50	Coffee break - Hall ILL 4
10:50-11:30	Daniel Harries	10:50-11:30	Arun Nandi
11:30-11:50	Yu Ogawa	11:30-11:50	Sylvain Prévost
11:50-12:10	Peter Košovan	11:50-12:10	Farewell
12:10 -14:00	Lunch - self-service at ILL/ESRF canteen	12:10-14:00	Lunch - self-service at ILL/ESRF canteen
14:00-17:00	Free or visit of ILL and ESRF	14:00-15:00	ILL's Colloquium - Olli Ikkala
17:00-19:30	Free		
19:30-22:00	Dinner at Restaurant Fantin Latour		

Programme

All talks will be given in the Chadwick Amphitheatre ILL

4 September 2018

11:30-12:30	Early registration (<i>mandatory for people eating at the canteen</i>)	
12:00-13:30	Lunch - self-service at ILL/ESRF canteen / free	
13:00-14:00	Registration	
14:00-14:30	Welcome address	Jean-Luc Putaux Giovanna Fragneto Jean Susini
14:30-15:10	Hybrid thermoreversible gels: polymer/self-assembled systems	Jean-Michel Guenet
15:10-15:30	Syndiotactic polystyrene fibers with antimicrobial properties	Christophe Daniel
15:30-15:50	Complexes of amylose with diols: polymorphism and factors affecting the crystal structure	Cong-Anh-Khanh Le
15:50-16:20	Coffee break - Hall ILL 4	
16:20-17:00	Influence of physico-chemical interactions on formation and properties of polymer nanoparticles	Petr Stepanek
17:00-17:20	Alternating sequence-controlled polymers with thermo-, pH- and selective ion-induced phase transition	Esther Cazares Cortes
Free evening		

5 September 2018

09:00-09:40	Self-assembling amyloid building blocks as scaffolds for rational material design	Anna Mitraki
9:40-10:00	Hierarchical nanotube self-assembly by DNA minor groove binding ligand DB921 via alkali halide triggering	Ryo Mizuta
10:00-10:20	Deuteration of biomolecules for neutron scattering studies	Trevor Forsyth
10:20-10:50	Coffee break - Hall ILL 4	
10:50-11:30	Coupling between protein and hydration water dynamics	Martin Weik
11:30-11:50	Presentation of the Partnership for Soft Condensed Matter (PSCM)	Giovanna Fragneto
11:50-12:10	Presentation of the Partnership for Structural Biology (PSB)	Florent Bernaudat
12:10-14:00	Lunch - self-service at ILL/ESRF canteen	
14:00-14:40	Solvent organisation and dynamics in self-assembled molecular gels	Marie Plazanet
14:40-15:00	Research on syndiotactic polystyrene complexes with simultaneous measurements of small-angle and wide-angle neutron scattering with FTIR spectroscopy	Fumitoshi Kaneko
15:00-15:20	Swelling and visco-elastic behaviour of wood in mixed solvents	Nicolas Le Moigne
15:20-15:50	Coffee break - Hall ILL 4	
15:50-16:30	Biobased polymer hydrogels. Challenges & strategies	Rebeca Hernández

16:30-16:50	Engineering of MoS ₂ quantum dots/PANI aerogel for high energy supercapaciator and hydrogen evolution electrocatalyst	Sujoy Das
16:50-17:10	Formation of recognition sites in an acrylic polymer by the molecular printing technique	Lamia Bedjaoui-Alachaer
17:30-20:00	Poster session / Wine & Cheese	

6 September 2018

9:00-9:40	Supramolecular polymer brushes for Janus-like nano-objects and hierarchical self-assemblies	Olli Ikkala
9:40-10:00	Experimental evidence of molecular relaxation processes in cellulose-amine physical complexes	Yoshiharu Nishiyama
10:00-10:20	Insights into cellulose solvation in organosolv mixtures: a molecular dynamics and quantum mechanics study	Sonia M. Aguilera-Segura
10:20-10:50	Coffee break - Hall ILL 4	
10:50-11:30	How do cosolutes stabilize polymers? From bridging to depletion attraction	Daniel Harries
11:30-11:50	Structure and molecular interactions of chitin crystallosolvates	Yu Ogawa
11:50-12:10	Adsorption of oligo-ampholytes to like-charged polyelectrolytes	Peter Košovan
12:10 -14:00	Lunch - self-service at ILL/ESRF canteen	
14:00-17:00	Free or visit of ILL and ESRF	
17:00-19:30	Free	
19:30-23:00	Dinner at Restaurant Fantin Latour	

7 September 2018

09:00-9:40	Adaptable polysaccharide hydrogels with reversible boronate ester crosslinks: control of the mechanical properties through the synthetic manipulation of the small molecule crosslinkers	Rachel Auzély
9:40-10:00	Hyaluronic – Pluronic mixed system: Depletion interaction between micelles triggered by the polyelectrolyte chain conformation	Isabelle Grillo
10:00-10:20	Efficient facilitated transport of lead and cadmium across a plasticized triacetate membrane mediated by organo-phosphorous carrier	Akkacha Mazari
10:20-10:50	Coffee break - Hall ILL 4	
10:50-11:30	Parity violation in supramolecular aggregation: Insights from optoelectronic properties	Arun Nandi
11:30-11:50	Opportunities and challenges for small-angle neutron scattering of polymers	Sylvain Prévost
11:50-12:10	Farewell	Jean-Luc Putaux
12:10-14:00	Lunch - self-service at ILL/ESRF canteen or sandwiches	
14:00-15:00	ILL's Colloquium (<i>optional for Polysolvat attendees</i>)	Olli Ikkala

List of posters

P1. Naima ABDELLAOUI, Zahra HIMEUR, Omar AROUS

The effect of crown-ethers additives on poly (2-[N,N diéthylaminoéthyle] methacrylate) (PDAEM) and cellulose triacetate (CTA) asymmetric dialysis membrane performance.

P2. Akkacha MAZARI, Mouhamed TRARI, Omar AROUS

Photo-electrodialysis combination system for Pb^{2+} removal using polymeric membrane/semiconductor

P3. Dounya MERAH, Ulrich MASCHKE, Lamia BEDJAOUI-ALACHAHER

Effect of crosslinking agent and nature of solvent on the swelling behavior of pIBOA-co-2-EHA.

P4. Meriem MIHOUB, Ulrich MASCHKE, Lamia BEDJAOUI-ALACHAHER, Salah HAMRI, Tewfik BOUCHAOUR

pH-responsive Interpenetrating polymeric network based on cellulose/ poly(HEMA): elaboration and swelling behavior.

P5. Nouria BOUCHIKHI, Salah HAMRI, Djahida LERARI, Ulrich MASCHKE, Fayçal DERGAL, Khaldoun BACHARI, Lamia BEDJAOUI-ALACHAHER,

Effect of several parameters on the kinetic of polymerization of hydroxyethyl acrylate (HEA) induced by visible light.

P6. Nico CARL, Klaus HUBER, Ralf SCHWEINS, Sylvain PREVOST

Self-assembly of block copolymers of two negatively charged polyelectrolytes and multivalent cations.

P7. Giuseppe Rosario DEL SORBO, Ingo HOFFMANN, Emanuel SCHNECK

Structural investigation of biopolyelectrolyte-surfactant complexes: Developments in the understanding of viscosity behaviour

P9. Assia Siham HADJ-HAMOU, Manel SERAY, Fayçal BENHACINE

Development of active films based on poly(butylene adipate-co-terephthalate) filled with silver-montmorillonite nanoparticles for food packaging use.

P10. Michael HÄRTLEIN, Martine MOULIN, Juliette DEVOS, Valérie LAUX, Trevor FORSYTH

Deuteration of biomolecules for neutron scattering studies.

P11. Hyeon-Gyun IM, Dong Jun KANG

Transparent moisture barrier using surface-modified nanoclay composite for OLED encapsulation.

P12. Hyeon-Gyun IM, Dong Jun KANG

Robust transparent protective hard-coating using physicochemically-incorporated silica nanoparticles and organosiloxanes.

P13. Cong-Anh-Khanh LE, Yu OGAWA, Luc CHOISNARD, Denis WOUESSIDJEWÉ, Jean-Luc PUTAUX

Crystal structure of V-amylose inclusion complexes: new developments and some surprises

- P14. Farid METREF**, Abderahmane OUARTLI, Samia CHEKROUN
Miscibility, thermal stability and non-isothermal decomposition kinetic of polymer blends based on poly(vinylchloride) and poly(methylmethacrylate-co-4-vinylpyridine)
- P15. Isabelle MORFIN**, Jérôme COMBET, Sylvie SPAGNOLI, Marie PLAZANET, Judith PETERS
Hydration of hyaluronan in electrostatic self-assemblies.
- P16. Arun K. NANDI**, Nabasmita MAITY
Effect of chain length alteration on the self-assembly of poly(ϵ -caprolactone) functionalized graphene quantum dots.
- P17. Wanda NAVARRA**, Olga SACCO, Vincenzo VAIANO, Vincenzo VENDITTO, Christophe DANIEL
Nanocomposite aerogels for removing water organic pollutants.
- P18. Kamal OUAAD**, Said DJADOUN, Chihab MEHAI
Morphology and thermal behavior of blends and nanoblends based on poly(styrene-co-allyl alcohol)/ cellulose acetate butyrate and an organically modified Maghnia bentonite.
- P19. Souad KADI, Kamal OUAAD**, Said DJADOUN
Morphology and thermal stability of cellulose acetate butyrate and poly (ethyl methacrylate) nanoblends.
- P20. Kristina WAGNER, Sylvain PREVOST**, Nico CARL, Matthias KARG
Influence of temperature and concentration on the solution phase behavior of poly(N-isopropylacrylamide) homopolymers.
- P21. Ralf SCHWEINS**, Franziska GROEHN, Giacomo MARIANI
Self-assembly of dendrimers and oppositely charged dyes as a function of solvent pH and salt content.

**ABSTRACTS OF
ORAL COMMUNICATIONS**

INVITED LECTURES

Hybrid thermoreversible gels: polymer/self-assembled systems

Jean-Michel GUENET

Institut Charles Sadron, CNRS, Strasbourg, France

email corresponding author: jean-michel.guenet@ics-cnrs.unistra.fr

We present in this talk three types of hybrid materials made up from covalent polymers and supramolecular polymers that form thermoreversible gels and therefore possess fibrillar morphology. Two main cases are shown: i) intermingled gel where the polymer gel and the organogel pervade one another [1], ii) sheathed or jacketed nanowires, where one component trigger the growth of the other by means of a heterogeneous nucleation process [2,3]. The polymers used are isotactic polystyrene, syndiotactic polystyrene, that form polymer-solvent compounds, and poly(3-butylthiophene-2,5-diyl) (P3BT), a semi-conducting polymer, while the self-assembling materials are bicopper-2-éthyle hexanoate complex, that pile up to form long filaments, OPV (oligo phenylene vinylene), that produces an organogel [4], and 3,5-bis-(5-hexylcarbamoylepentyloxy)-benzoic acid decyl ester (BHPB-10), that forms nanotubes [5]. The intermingled network is made up with isotactic or syndiotactic polystyrene and OPV in a common solvent. The encapsulated system consists of the filaments of bicopper-2-ethyl hexanoate complex, an antiferromagnetic molecule, encapsulated in isotactic polystyrene fibrils [2]. The encapsulation is seen to impart new magnetic properties, namely the magnetic susceptibility is no longer 0 at $T = 0$ K [6]. Sheathed systems comprise isotactic polystyrene fibrils sheathed by BHPB-10 nanotubes [4,5], as well as (P3BT) jacketed by the same nanotubes. In the latter case insulated nanowires are obtained [7]. Results on the formation thermodynamics, the morphology and the molecular structure will be presented. All the experimental results show that a high degree of compatibility exists between all the components thus allowing one to prepare materials where one component is finely dispersed within the other. Their functional properties as studied by SQUID and conducting AFM (C-AFM) will also be presented.

1. D. Dasgupta, S. Srinivasan, C. Rochas, et al., *Langmuir* 25 (2009), 8593.
2. D. Lopez, J.-M. Guenet, *Eur. Phys. J. B*12 (1999), 405.
3. D. Dasgupta, Z. Kamar, C. Rochas et al., *Soft Matter* 6 (2010), 3576.
4. A. Ajayaghosh, S.J. George, *J. Am. Chem. Soc.*123 (2001), 5148.
5. N. Díaz, F.-X. Simon, M. Schmutz et al., *Angew. Chem. Int. Ed.* 44 (2005), 326.
6. A. Boulaoued, J.-L. Bantignies, R. Le Parc et al., *Langmuir* 32 (2016), 13193.
7. G. Raj, A. Boulaoued, J. Lacava, L. Biniek et al., *Adv. Electr. Mat.* (2017), 1600370.

Influence of physico-chemical interactions on formation and properties of polymer nanoparticles

Petr STEPANEK

Institute of Macromolecular Chemistry, Czech Academy of Sciences, Prague

email corresponding author: stepanek@imc.cas.cz

Nanoprecipitation is a very useful technique for encapsulation of hydrophobic species in nanoparticles dispersed in aqueous systems. In particular it enables encapsulation of a hydrophobic drug in submicron particles and thereby effectively increases its water solubility but the technique is more generally applicable in various areas of physics, medicine and chemistry. A key factor that determines the functionality of NPs is their size and the distribution of sizes that limits or enhances various applications. Various approaches to control the size of nanoparticles will be discussed. This includes macroscopic nanoprecipitation as well as nanoprecipitation in microfluidic channels, effects of temperature, concentration, ionic strength and quality of the solvents. Nanoparticles can be prepared with or without surfactants; in the latter case influence of the nature of the surfactant will be demonstrated by comparing neutral and charged surfactants, and low-molecular-weight and polymeric surfactants. Kinetics of nanoprecipitation will be discussed on the basis of time-resolved SAXS measurements. Interaction of the polymer with the solvents as well as the miscibility of the solvents used has an important effect on the final size and properties of nanoparticles. Generally the nanoparticles are not compact but have an inner porosity (that will be quantified), which is a convenient structural feature for loading of the molecules to be encapsulated.

The work was supported by the Ministry of Education, Youth and Sports of CR within the National Sustainability Program I (NPU I), Project POLYMAT LO1507 and by the Grant Agency of the Czech Republic, grant 16-02870S.

Self-assembling amyloid building blocks as scaffolds for rational material design

Anna MITRAKI¹, Joseph M. JAKUBOWSKI², Antonio L. LLAMAS-SAIZ³, Phanourios TAMAMIS², Matthew W. BOWLER⁴, Edward P. MITCHELL⁵, Trevor V. FORSYTH⁶, Estelle MOSSOU⁶, Apostolos CHATZOUZIS⁷, Marianna KOTZABASAKI⁷, Mark J. VAN RAAIJ⁸, Chrysanthi Pinelopi APOSTOLIDOU¹, Mateo SEOANE-BLANCO⁸, Asuka A. ORR², Vamshi R. JONNALAGADDA², Chrysoula KOKOTIDOU¹

¹ *Department of Materials Science and Technology, University of Crete and IESL/FORTH*

² *Artie McFerrin Department of Chemical Engineering, Texas A&M University*

³ *X-Ray Unit, RIAIDT, CACTUS building, Campus Vida, University of Santiago de Compostela*

⁴ *European Molecular Biology Laboratory, Grenoble Outstation*

⁵ *European Synchrotron Radiation Facility, Grenoble*

⁶ *Institut Laue-Langevin, Grenoble*

⁷ *Department of Materials Science and Technology, University of Crete*

⁸ *Departamento de Estructura de Macromoleculas, Centro Nacional de Biotecnologia (CSIC)*

email corresponding author: mitraki@materials.uoc.gr

Self-assembling peptides gain increasing interest as scaffolds for novel bionanomaterials; rationally designed self-assembling building blocks are especially attractive. We have been focusing on modular designs that consist of a central ultrashort amphiphilic motif derived from the adenovirus fiber shaft. This central amphiphilic motif can be further modified with amino acids targeted for various functionalities. The designer peptides self-assemble into fibrils that are structurally characterized with Transmission Electron Microscopy, Scanning Electron Microscopy and X-ray fiber diffraction; these fibrils were targeted to bind to metal nanoparticles, silica, calcium, and more recently, cells [1]. We have been using a combination of computational and experimental approaches towards rational designs. More recently we have reported that the YATGAIIGNII sequence from the HIV-1 gp120 V3 loop self-assembles into amyloid fibrils of which the first three and the last two residues are outside the GAIIG amyloid core [2]. We postulate that this sequence with suitable selected replacements at the flexible positions can serve as a designable scaffold for amyloid-based materials. Such short self-assembling peptides that are amenable to computational design offer open-ended possibilities towards multifunctional bionanomaterial scaffolds of the future.

1. G. Deidda et al., *ACS Biomater. Sci. Eng.* 3 (2017), 1404-1416.
2. C. Kokotidou et al., *FEBS Lett.* 592 (2018), 1777-1788.

Coupling between protein and hydration water dynamics

Martin WEIK¹, Giorgio SCHIRO¹, Bente VESTERGAARD², Tilo SEYDEL¹, Michael HARTLEIN¹, Michaela ZAMPONI³, Martine MOULIN¹, Annette LANGKILDE², Yann FICHOU⁴, Kevin POUNOT¹

¹ *Institut de Biologie Structurale, Grenoble*

² *University of Copenhagen*

³ *Heinz Maier-Leibnitz Zentrum*

⁴ *University of California, Santa Barbara*

email corresponding author: martin.weik@ibs.fr

As molecular workhorses, proteins fulfill a multitude of tasks that keep the complex machinery in biological cells alive. In order to be biologically active, most soluble proteins require their surface to be covered with water. This so-called hydration water is generally acknowledged to enable a protein to undergo the internal motions that are so fundamental for its capacity to fulfill a specific biological function. Incoherent neutron scattering (INS) in combination with selective deuterium labelling is a powerful tool that puts the focus either on protein or on water motions on the ns-ps time scale and allows their dynamic coupling to be studied. In particular, it is the translational diffusion of hydration-water molecules on the protein surface that enables functionally-relevant motions [1]. We have recently started focusing on the hydration-water dynamics of those proteins that can form the pathological fibers involved in so-called protein aggregation diseases, such as tau (Alzheimer's) and α -synuclein (Parkinson's). So far, evidence has been found that hydration water mobility is enhanced around tau amyloid fibers, a finding that identifies hydration water entropy as a potentially universal driving force behind fiber formation [2].

1. G. Schiro, Y. Fichou, F.X. Gallat et al., *Nat. Comm.* 6 (2015), 6490.

2. Y. Fichou, G. Schiro, F.X. Gallat et al., *Proc. Natl. Acad. Sci.* 112 (2015), 6365-6370.

Solvent organisation and dynamics in self-assembled molecular gels

Isabelle MORFIN¹, Marie PLAZANET¹, Miguel A. GONZALEZ², Sylvie SPAGNOLI¹

¹ *Laboratoire Interdisciplinaire de Physique, Grenoble, France*

² *Institut Laue-Langevin, Grenoble, France*

email corresponding author: marie.plazanet@univ-grenoble-alpes.fr

Physicals gels formed by low molecular weight organic gelators (LMMOG) are composed of a rigid network formed by the gelators, in which is trapped a large quantity of solvent. Gathering properties of both liquids and solids, they find applications as functionalized nanomaterials in diverse domains, although applications suffer several limitations, such as the unexpected collapse after some time or the difficulty to predict gelation ability of new molecules. The subtle interplay of the different forces exerted between the solvent and gelators enable the gels to reversibly assemble in a restricted temperature range in a complex structure that depends on the solvent. The interface between gelators and solvent is soft and ill-defined. Because of the intrinsic complexity, at the molecular level, of the structural organization and the dynamics, these materials are quantitatively studied with difficulty. In this context, we undertook the study of the microscopic dynamics in a model physical molecular gel, methyl-4,6-O-benzylidene- α -D-mannopyranoside (α -manno) [1] in water and toluene are probed by neutron scattering [2] and Transient Grating Spectroscopy [3]. The α -manno is an amphiphilic gelator that adopts different organizations in both solvents. We were able to distinguish, on a timescale from a few ps to few ns, several dynamical populations of solvent molecules in interaction with the rigid network formed by the gelators. We found that only few toluene molecules per gelator participate to the network which is formed by hydrogen bonding between the gelators' sugar moieties. In water, however, the interactions leading to the solid network assembly are weaker and each gelator forms a tens of hydrogen bonds with the surrounding water molecules, that are stable over few hundreds of ps only. Eventually, the gelator network dynamics can be distinguished just before the melting when its characteristic relaxation time enters the ns timescale. This study shows that quantitative information on the behaviour of solvent confined in a molecular gel can be obtained, also relevant to diffuse interfaces as often encountered in soft matter systems.

1. O. Gronwald O., S. Shinkai S., *Chem. Eur. J.* 7 (2001), 4328-4334.
2. S. Spagnoli, I. Morfin, M.A. Gonzalez et al., *Langmuir* 31 (2015), 2554-2560.
3. I. Morfin, S. Spagnoli, C. Rambaud et al., *Phil. Mag.* (2016), 809-815.

Biobased polymer hydrogels. Challenges & strategies

Rebeca HERNÁNDEZ

Instituto de Ciencia y Tecnología de Polímeros

email corresponding author: rhernandez@ictp.csic.es

The employment of biobased polymers, specifically, those extracted from the biomass (polysaccharides such as chitosan, alginate or agarose and proteins such as gelatin) is of particular interest for the development of biomedical applications. This is motivated on the one hand by the fact that many biobased polymers are able to assemble in water in response to different stimuli (pH, temperature or ionic concentration) to give rise to hydrogels in the form of macro, micro and nanogels. On the other hand, their intrinsic characteristics, biocompatibility and biodegradation properties make them suitable for applications in drug delivery or tissue engineering among others. In this communication, an overview of the research done in our group regarding hydrogels obtained from biobased polymers, structure-properties relationship and their biomedical applications will be presented. It concerns in particular the preparation of nanocomposite hydrogels in which the polysaccharide acts as encapsulating matrix or as template for the synthesis of metallic nanoparticles, combination with stimuli responsive hydrogels to obtain dual responsive interpenetrating polymer hydrogels or multilayer combinations obtained through electrostatic interactions between polyelectrolytes. Results on the influence of the structural organization of nanoparticles within polysaccharide hydrogels as determined through synchrotron techniques onto rheological and functional properties will be shown [1]. Finally, some selected applications in controlled drug release and magnetic hyperthermia will be presented [2,3].

1. R. Hernandez, R. et al., *Soft Matter* 6 (2010), 3910-3917.
2. T.C.d. Santos et al., *Europ. Polym. J.* 99 (2018), 456-463.
3. V. Zamora-Mora et al., *Carbohydr. Polym.* 157 (2017), 361-370.

Supramolecular polymer brushes for Janus-like nano-objects and hierarchical self-assemblies

Olli IKKALA

Aalto University, Molecular Materials, Department of Applied Physics, Aalto

email corresponding author: olli.ikkala@aalto.fi

Polymer conformations and self-assemblies can be modularly controlled using bottlebrush-like architectures, where the side chain brushes are physically bonded to the polymer backbones. As the side chain brush molecules can be considered as solvents, the architecture is a specific case of polymer-solvent complexes. Competition between attractive and repulsive interactions is crucial for the self-assemblies. Here we describe recent approaches towards complex architectures and self-assemblies. We first describe triblock terpolymers polystyrene-block-poly(4-vinylpyridine)-block-poly(tert-butyl methacrylate) where the central block has been hydrogen bonded using rodlike 4-(4-pentylphenylazo)phenol molecules based on the relatively strong phenol-pyridine hydrogen bonds. It forms complicated ternary self-assemblies where the supramolecular phase forms cylindrical or lamellar confined self-assemblies within the interfaces between the polystyrene and poly(tert-butyl methacrylate) domains. Quaternization of pyridines and solvent manipulation allows cleaving of self-assembled Janus-objects. Halogen bonding has recently received considerable attention in supramolecular chemistry. Halogen bonding of rod-like 1-iodoperfluoroalkanes to star-shaped ethylene glycol-based low molecular weight polymers with amine hydrochloride end-groups allows smectic nanometric structures aligned up to micrometer length scale without external direction. Finally, we show that halogen bonding rod-like 1,8-diiodoperfluorooctane with the pyridines of polystyrene-block-poly(4-vinyl pyridine) allows hierarchical self-assemblies and colloidal supramolecular fibers stabilized by halogen bonds.

1. P. Hiekkataipale, T.I. Löblich, M. Poutanen et al., *Polymer* 107 (2016), 456.
2. N. Houbenov, R. Milani, M. Poutanen et al., *Nat. Commun.* 5 (2014), 4043.
3. R. Milani, N. Houbenov, F. Fernandez-Palacio et al., *Chem* 2 (2017), 417.

How do cosolutes stabilize polymers? From bridging to depletion attraction

Daniel HARRIES, Liel SAPIR

The Hebrew University, Jerusalem

email corresponding author: daniel.harries@mail.huji.ac.il

Solution composition is known to strongly influence the stable state of macromolecules, with important practical applications ranging from colloidal dispersions to solvated synthetic polymers or proteins. Cosolutes with different affinities to specific macromolecular states can shift equilibrium towards the thermodynamically preferred state with lower free energy. Solutes preferentially excluded from macromolecules drive depletion forces and stabilize the compact macromolecular state. To contrast, cosolutes preferentially included around the macromolecule usually destabilize the compact state, effectively stabilizing the extended state of the macromolecule, as in the case of protein denaturants. However, in certain cases preferentially included cosolutes stabilize another compact state through bridging interactions. By using a simple mean field model that contains only few interaction parameters, we demonstrate the possible mechanisms by which preferentially interacting cosolutes affect macromolecules. Specifically, depletion interactions, bridging stabilization, and macromolecular destabilization, all emerge in a single model as concentration, interaction parameters, and cosolute size are varied. The theory also highlights the possible sources of energetic and entropic contributions to these mechanisms of stabilization.

Adaptable polysaccharide hydrogels with reversible boronate ester crosslinks: control of the mechanical properties through the synthetic manipulation of the small molecule crosslinkers

Rachel AUZELY

CERMAV-CNRS, Univ. Grenoble Alpes, Grenoble

email corresponding author: rachel.auzely@cermav.cnrs.fr

Adaptable hydrogels, built through dynamic covalent bonds, have recently emerged as a promising platform for tissue engineering and regenerative medicine [1,2]. The dynamic nature of the crosslinks in these polymer networks enables them to have shear-thinning (viscous flow under shear stress) and self-healing (recovery upon relaxation) characteristics. Therefore, adaptable hydrogels can be used as injectable scaffolds for minimally invasive delivery of cells and in the filling of irregular defects. The fast and stable bond formation between boronic acids and sugars to form boronate esters has been successfully used by our group for forming such injectable and self-healing hydrogels from hyaluronic acid (HA), a polysaccharide that is ubiquitous in the human body [3]. In these networks, gel properties are closely tied to the structure of the small molecule crosslinkers, i.e. the phenylboronic acid (PBA) and sugar moieties grafted on HA. Given the advantages offered by such hydrogels for biomedical applications, we sought to gain a better understanding of the relationships between molecular and hydrogel network properties, to control the macroscopic mechanical properties through the synthetic manipulation of the small molecule crosslinkers. In this presentation, we will show how the binding mode of boronic acids to saccharide moieties affects the mechanical properties of the HA-based hydrogels, which paves the way for the rational design of injectable hydrogels with tailored mechanical properties.

1. D. L. Taylor, M. in het Panhuis, *Adv. Mater.* 28 (2016), 9060-9093.
2. H. Wang, S. C. Heilshorn, *Adv. Mater.* 27 (2015), 3717-3736.
3. D. Tarus, E. Hachet, L. Messenger et al., *Macromol. Rapid Commun.* 35 (2014), 2089-2095.

Parity violation in supramolecular aggregation: Insights from optoelectronic properties

Arun K. NANDI, Arnab SHIT, Pousali CHAL

Indian Association for the Cultivation of Science, Kolkata

email corresponding author: psuakn@iacs.res.in

The Maxwell electromagnetic equations obey parity (P), however, Wu et al, first proved a clear violation of parity conservation in the beta decay of cobalt-60 [1]. It is now widely believed that in physical systems having weak interactions parity violation is possible. Now the question is if it is true in physical systems why not in chemical systems, particularly where there is self-aggregation via weak physical interactions. In the contemporary science, it is believed that supramolecular chiral structures (left-or right-handed and P-or M-helices) emanating from enantiomeric (L- or D-enantiomers) chiral building blocks would have identical physical and chemical properties [2]. Here we show that the chiral perylenebisimide (PBI) derivatives containing enantiomeric L- or D-phenylalanine self-assemble to mirror image helical supramolecular structures with dissymmetric energy states. We have synthesized PBI derivatives with chiral L- and D-phenylalanine at the imide positions and designated as PPAL and PPAD. Surprisingly, they exhibit different optoelectronic characteristics in the supramolecular aggregated state in chlorinated solvents. A detailed analysis of these systems by microscopy, X-ray scattering and spectroscopy in different and mixed solvents reveal that PPAL affords compact self-assembled structure with long-range order than PPAD. Thus, with increase of concentration the aggregated molecules gives smaller scope to interact with the added molecule due to rotational restriction etc., thus with increasing concentration the weak interaction becomes weaker yielding different optoelectronic properties between D and L-isomers in the self-assembly, causing parity violation. These studies may provide a great impetus in understanding the origin of the evolutionary conserved L-amino acids in nature and will have important impact towards designing efficient optoelectronic devices with chiral organic supramolecular materials.

1. C.S. Wu et al., *Phys. Rev.* 105 (1957), 1413.
2. M.B. Avinash, T. Govindaraju, *Adv. Funct. Mater.* 21 (2011), 3875–3882.

**ABSTRACTS OF
ORAL COMMUNICATIONS**

SHORT TALKS

Syndiotactic polystyrene fibers with antimicrobial properties

Christophe DANIEL, Chiara BOTTA, Antonietta COZZOLINO, Paola RIZZO, Gaetano GUERRA

Dipartimento di Chimica e Biologia, Università degli Studi di Salerno

email corresponding author: cdaniel@unisa.it

Syndiotactic polystyrene (sPS) is a stereoregular polymer with a very complex polymorphic behaviour capable of forming co-crystals (molecular-complex crystalline phases) with many low molecular mass guests. In particular the formation of co-crystalline forms with optically active molecules (chromophore, fluorescent, photoreactive), magnetic and polar molecules has been reported and films presenting s-PS/active-guest co-crystalline phases have been proposed as advanced optical, ferroelectric, and paramagnetic materials [1]. The formation of s-PS co-crystalline phases with carvacrol, a natural antimicrobial, has been also recently reported [2] and it has been shown that the inclusion of the antimicrobial molecules within the co-crystalline phase allows a slow antimicrobial release which may assure a long-term antimicrobial efficiency. In this contribution different aspects relative to the preparation and the crystalline structure of s-PS fibers with co-crystalline phases containing different natural microbial molecules such as eugenol, thymol will be presented and discussed. The antimicrobial desorption properties as well as the antimicrobial activity tests of these materials will be also reported.

1. G. Guerra et al., *J. Polym. Sci., Part B: Polym. Phys.* 50 (2012), 305-322.
2. A. R. Alburnia et al., *J. Polym. Sci., Part B: Polym. Phys.* 52 (2014), 657-665.

Complexes of amylose with diols: polymorphism and factors affecting the crystal structure

Cong-Anh-Khanh LE¹, Denis WOUESSIDJEWE², Luc CHOISNARD², Jean-Luc PUTAUX¹

¹ CERMAV-CNRS, Grenoble

² DPM, Univ. Grenoble Alpes, CNRS, Grenoble

email corresponding author: le@cermav.cnrs.fr

Amylose forms crystallosolvates with a large variety of small molecules [1]. This so-called “V-amylose” occurs as single helices and the guest molecules can be located inside the helices, in-between or both [2]. We have studied the morphology (TEM) and crystal structure (X-ray and electron diffraction) of V-amylose complexed with a series of diols with different chemical structures (i.e. 1,3-butanediol, 1,4-butanediol and 1,6-hexanediol). The complexes were prepared from 0.1 wt% aqueous amylose solutions in the form of lamellar single crystals using various concentrations of diols and crystallization temperatures. In the wet state, four allomorphs were identified, containing 6- or 7-fold amylose single helices organized into hexagonal or orthorhombic unit cells. Upon drying, a structural transition was observed for each allomorph, resulting in the formation of three other pseudo-hexagonal or pseudo-tetragonal crystalline forms. A transition from a 7-to a 6-fold helical conformation was also observed. Some features of the complexing diols were shown to be decisive in controlling the resulting crystal structures, such as the geometry of the carbon chain (branched or linear, chain length) and the position of the hydroxyl groups. By adequately controlling the crystallization temperature and diol concentration, a given diol could induce the formation of several distinct allomorphs.

We thank LabEx Arcane (Grenoble) for the financial support of C.A.K. Le’s PhD, and the ICMG-NanoBio platform (Grenoble) for granting access to the Electron Microscopy facility.

1. D. Lourdin, J.-L. Putaux, G. Potocki-Véronèse, C. Chevigny et al., In “*Starch-Metabolism and Structure*”, Y. Nakamura ed., Springer Japan, 2015, pp 61-90.
2. J.-L. Putaux, Y. Nishiyama, K. Mazeau et al., *Macromol. Symp.* 303 (2011), 1-9.

Alternating sequence-controlled polymers with thermo-, pH- and selective ion-induced phase transition

Esther CAZARES CORTES¹, François TOURNILHAC¹, Makoto OUCHI², Bogdan TARUS¹, Benjamin BAKER¹

¹ *Lab. Matière Molle et Chimie - ESPCI Paris*

² *Department of Polymer Chemistry, Kyoto University*

email corresponding author: esther.cazares-cortes@espci.fr

Stimuli-responsive polymers are capable of modifying their chemical/physical properties upon expo-sure to different stimuli (temperature, pH, ionic strength). On another hand the currently emerging development of sequence-controlled copolymerization strategies open up opportunities for the design of new generations of smart polymers [1]. Methods like iterative single addition of monomers by living polymerization effectively give access to sequence-controlled polymers but with low yield / efficiency ratios. Alternate approaches through cyclo- and template-polymerization [2] of cleavable multi-vinyl monomers are potentially suitable to synthesize larger quantities of sequence polymers making it possible to envision practical applications in the field of materials. A new alternating sequence-controlled copolymer has been synthesized by cyclopolymerization of divinyl monomers with hemiacetal ester cleavable pendant groups. After cleavage of these groups, an alternating sequence (AS) of carboxylic acid and hydroxide groups was obtained [3]. Here, we present the synthesis of this AS-copolymer and we investigate the influence of the temperature, the pH and ions on the polymer solution behavior, using a laser scattering and diode detection system. In an organic solvent (1,2-dimethoxyethane), the alternating sequence of two functional groups provided a lower critical solution temperature (LCST) around 22°C. In water, the LCST is only observed at low pH conditions (pH<3, LCST from 25 to 38°C). Moreover, this copolymer shows a selective ion-induced LCST-transition in response to K⁺ and Ag⁺ cations; while in the presence of Na⁺, Cu²⁺ and Li⁺ no phase transition was observed. Molecular dynamic (MD), SANS and IR spectroscopy studies have been completed to elucidate the LCST behavior. This alternating sequence copolymer is a promising new candidate for sensors and membranes for selective cation recognition.

1. J.-F. Lutz, M. Ouchi, D.R. Liu, M. Sawamoto, *Science* 341 (2013), 1238149.
2. Y. Hibi et al., *Polym. Chem.* 2 (2011), 341–347.
3. M. Ouchi, et al., *Angew. Chem. Int. Ed.* 55 (2016), 14584–14589

Hierarchical nanotube self-assembly by DNA minor groove binding ligand DB921 via alkali halide triggering

Ryo MIZUTA¹, Edward P. MITCHELL², Trevor V. FORSYTH³, Michael HAERTLEIN³, Patrice RANNOU⁴, Ralf SCHWEINS³, Stephen NEIDLE⁵, W. David WILSON⁶, David BOYKIN⁶, Abdelbasset A. FARAHAT⁷, Estelle MOSSOU³, Deeksha MUNNUR⁸, Adam ROUND⁹, Theyencheri NARAYANAN², Jessica WEBSTER³, Wai Li LING¹⁰, Juliette DEVOS³

¹ *University of Cambridge*

² *European Synchrotron Radiation Facility, Grenoble*

³ *Institut Laue-Langevin, Grenoble*

⁴ *CEA, INAC-SyMMES, CNRS, Université Grenoble Alpes*

⁵ *University College London*

⁶ *Georgia State University*

⁷ *Mansoura University*

⁸ *University of Oxford*

⁹ *European XFEL, Hamburg*

¹⁰ *Institut de Biologie Structurale, Grenoble*

email corresponding author: rm832@cam.ac.uk

Self-assembling systems comprise of materials that enable complex structures to form from molecular building blocks without external impetus. In particular, the chemical and physical properties of the self-assembled structure are encoded in the corresponding characteristics of the building blocks, thereby offering the potential for rationally designed materials with properties that are tailored to specific applications. However, the assembly process is often driven by a subtle interplay of multiple intermolecular forces such as electrostatics, hydrogen bonding, and solvent interactions. Any control and rational design is thus predicated on a thorough understanding of these fundamental driving interactions. We describe a novel self-assembling, supramolecular nanotube system formed by a heterocyclic cationic molecule, DB921 [1]. Our structural characterisation work via small-angle X-ray/neutron scattering (SAXS/SANS) along with cryo-transmission electron microscopy, evidence a hierarchical assembly mechanism via helical intermediates that is triggered by the addition of alkali halide salts. It is thus proposed that the primary driving interactions for the assembly are ionic interactions and the formation of aromatic pi-pi stacking interactions. Importantly, it is found that this alkali halide provides a convenient handle for modulating key properties of the system. Our time-resolved SAXS studies highlight a critical anion concentration above which the rate of self-assembly is greatly enhanced, whilst altering the choice of the halide anion between chloride and bromide results in different nanotube diameters.

1. R. Mizuta et al., *Nanoscale* 10 (2018), 5550–5558.

Deuteration of biomolecules for neutron scattering studies

Michael HÄRTLEIN, Martine MOULIN, Juliette DEVOS, Valérie LAUX, Trevor FORSYTH

Institut Laue-Langevin, Grenoble

email corresponding author: haertlein@ill.fr

Neutron scattering studies offer unique insights to biopolymers. This results mainly from the fact that the scattering power for neutrons of hydrogen is comparable to the other atoms typically found in biological macromolecules, contrasting strongly with the situation for X-rays where hydrogen atoms scatter very weakly. This is of crucial importance given that about half of the atoms in biological molecules are hydrogen and that they are often highly significant to biological structure and function. Deuteration, the replacement of hydrogen atoms by the stable isotope deuterium is a powerful method for the investigation of the structure and dynamics of biomolecules by means of neutron scattering. The pronounced differences in the scattering cross sections between hydrogen- and deuterium containing molecules allows to highlight parts of molecular complexes by neutron scattering methods such as small-angle neutron scattering or neutron reflectometry. In neutron crystallography perdeuteration allows the work with smaller crystals and facilitates the interpretation of nuclear density maps. The Institut Laue-Langevin Life Sciences Group operates a Deuteration Laboratory (D-Lab) as a platform within the *Partnership for Structural Biology*. Protocols for the complete, partial or selective *in vivo* deuteration of biomolecules have been developed. Generally, *Escherichia coli* or *Pichia pastoris* high cell-density fermenter cultures are used for the deuteration of recombinantly expressed proteins, nucleic acids and lipids such as phosphatidylcholine or cholesterol. Deuterated biomolecules produced in the ILL D-lab were essential for recently published neutron scattering work in high impact journals.

Access to the ILL / PSB Deuteration platform is via a peer review procedure, details of which can be found at: <http://www.ill.fr/deuteration>.

The Partnership for Soft Condensed Matter (PSCM)

Yuri GERELLI, Giovanna FRAGNETO

Institut Laue-Langevin, Grenoble

email corresponding author: fragneto@ill.fr

The Partnership for Soft Condensed Matter is a scientific and technical platform supporting ambitious large-scale soft matter research projects related to nanomaterials, environmental and energy sciences, biotechnology and related fields. The PSCM facilitates a deeper exploitation of state-of-the-art neutron instruments and synchrotron beamlines in combination with on-site specialised sample preparation and characterisation facilities. Together these enable cutting-edge experiments for the investigation of the structure and dynamics of bulk and interfacial soft matter and related systems. Located on the EPN Science Campus in Grenoble, France, the PSCM is a joint initiative of the European Synchrotron Radiation Facility (ESRF) and the Institut Laue-Langevin (ILL). Academic and industrial organisations can join the PSCM as Collaborative Partner Organizations (CPOs) to pursue fundamental and applied soft matter research in their specific area of interest. All ILL and ESRF soft matter studies can benefit from the PSCM equipment and expertise. In this talk the initiative will be presented including examples of the science that it has enabled in the last few years at the ILL.

Web: <http://www.epn-campus.eu/users/partnership-for-soft-condensed-matter-pscm/>

The Partnership for Structural Biology (PSB)

Florent BERNAUDAT

European Synchrotron Radiation Facility

email corresponding author: florent.bernaudat@esrf.fr

The Partnership for Structural Biology (PSB) was established by a Memorandum of Understanding in 2002 by the European Molecular Biology Laboratory (EMBL), the European Synchrotron Radiation Facility (ESRF), the Institut Laue Langevin (ILL) and the Institut de Biologie Structurale (IBS) to provide a unique environment for state-of-the-art integrated structural biology, and comprises about 300 active scientists (staff scientists, students and post-docs and technicians). This presentation will introduce the activities of the partnership and the wide range of technological platforms available in the PSB.

Web: www.psb-grenoble.eu

Research on syndiotactic polystyrene complexes with simultaneous measurements of small-angle and wide-angle neutron scattering with FTIR spectroscopy

Fumitoshi KANEKO¹, Zhaomin HOU², Masayoshi NISHIURA², Shinichi TAKATA³, Hiroki IWASE⁴, Maria Maddalena SCHIAVOVE⁵, Aurel RADULESCU⁵

¹ *Department of Macromolecular Science, Osaka University*

² *Organometallic Chemistry Laboratory, RIKEN Cluster for Pioneering Research*

³ *Materials and Life Science Division, J-PARC Center*

⁴ *Neutron Science and Technology Center, CROSS*

⁵ *Jülich Centre for Neutron Science at MLZ*

email corresponding author: toshi@chem.sci.osaka-u.ac.jp

Syndiotactic polystyrene (sPS) has a unique property to form molecular complexes with a variety of chemical compounds, from low mass molecules to polymeric compounds. The guest molecules are stored in the cavities surrounded by the phenyl side groups of sPS. The sPS complex can be generated not only as crystalline solid states but also as gel states from solutions and glass samples. Under certain conditions, the sPS complex exhibits some characteristic structural changes, such as the substitution of the guest molecules and the transformation to a crystal polymorph of sPS ejecting the guest molecules from the cavities. Small angle neutron scattering (SANS) is a versatile and convenient method to investigate the higher order structure of molecular assembly systems. It is a quite suitable tool to follow and analyze the structural changes and formation process of sPS complexes; by exploiting the significant difference in scattering length between fully deuterated and protonated compounds we can deduce the information how the guest molecules are distributed in the sPS complex system. In order to assist the analysis of SANS data, we developed a simultaneous SANS/FTIR measuring system by employing the KWS-2 diffractometer at MLZ Germany [1,2], which is able to add the molecular level information such as conformation and concentration. Furthermore, we recently introduced this methodology to a neutron scattering instrument covering a wider scattering angle range (BL-15 Taikan at JPARC, Japan), which makes it possible to access the hierarchical structures in polymer complexes, from the higher order structures to the interior structure within the crystal lattice. We have applied the simultaneous measurement method to the studies on the temperature dependent structure changes of sPS cocrystals and the sPS gelation process from binary-solute solutions.

1. F. Kaneko, N. Seto et al., *Chem. Lett.* 44 (2015), 497–499.
2. F. Kaneko, N. Seto et al., *J. Appl. Cryst.* 49 (2016), 1420–1427.

Swelling and visco-elastic behaviour of wood in mixed solvents

Julie BOSSU¹, Melissa POLINI², Nicolas LE MOIGNE³, Stéphane CORN³, Philippe TRENS¹, Quoc-Khôi TRAN², Francesco DI RENZO¹

¹ *Institut Charles Gerhardt Montpellier*

² *Atelier Régional de Conservation ARC-Nucléart, CEA-Grenoble*

³ *Centre des Matériaux des Mines d'Alès, IMT Mines Alès, Université de Montpellier*

email corresponding author: nicolas.le-moigne@mines-ales.fr

The relevance of solvents and technical treatments used for wood-based products requires a proper identification of the specific role of each solvent on wood biopolymers to better understand their influence on wood properties. In particular, wood impregnated with aqueous solutions of organic solvents has shown to give rise to a stronger swelling than that observed in pure water. This unexplained phenomenon, described as “hyperswelling”, can hardly be elucidated because of the complexity of wood microstructure. In this study, the effect of the impregnation of aqueous solutions of ethanol of variable concentrations on the physico-mechanical properties of poplar wood has been investigated [1]. The sorption behaviour of veneer sapwood samples has been analyzed by vapour sorption gravimetry, dynamic mechanical analysis and optical microscopy monitoring. Pure water and ethanol showed two really contrasting sorption behaviours. Despite comparable amounts sorbed, ethanol leads to a lower swelling and a very limited softening, suggesting different affinities of ethanol and water for wood biopolymers. With mixed solutions, larger swelling and stronger variations in visco-elastic behaviour than in pure solvents were observed, confirming the synergistic effect of water/ethanol mixtures on wood cells physico-mechanical properties. Microscopic observations evidenced that ethanol, both alone and in aqueous solutions, generates intercellular decohesion and disbonding of the wood cell wall layers in the middle lamella region. These observations are consistent with a mechanism of partial solubilisation by ethanol of phenolic compounds such as lignins, which leads to a release of constraints and allows a stronger swelling of the cell wall polysaccharides by water. Such phenomenon is likely to be at the origin of the hyperswelling observed in mixed solutions. Finally, the methodologies developed in this study opens interesting perspectives for the analysis of the swelling, visco-elastic behaviour and stability of technical wood-based products in controlled environmental conditions (relative humidity, temperature). In this regard, dynamic mechanical analysis in controlled relative humidity atmosphere was conducted on pine and beech wood impregnated with polymers having different glass transition temperature and hydrophilicity. The results showed contrasted visco-elastic behaviour according to relative humidity and wood–polymer systems.

1. J. Bossu, N. Le Moigne, S. Corn et al. *Wood Sci. Technol.* 52 (2018), 987–1008.

Engineering of MoS₂ quantum dots/PANI aerogel for high energy supercapaciator and hydrogen evolution electrocatalyst

Arun. K. NANDI, Sujoy DAS

Indian Association for the Cultivation of Science, Kolkata

email corresponding author: s.das648@gmail.com

The low conductivity of MoS₂ presents a huge barrier for the exploitation of its supercapacitor electrode application and hydrogen evolution reaction (HER) catalyst. To alleviate this difficulty, we have synthesized MoS₂ quantum dots (QDs) having greater quantity of catalytic edge sites by breaking up bulk MoS₂ sheet using the solvent exfoliation technique. The synthesized MoS₂ QDs are embedded into polyaniline (PANI)-N,N'-dibenzoyl-L-cystine (DBC) aerogel matrix for high energy supercapacitor and HER catalyst. Here, conductive PANI matrix are prepared by in situ polymerization of aniline where DBC acts as a gelator, dopant, and cross-linker. The DBC-PANI aerogel shows conductivity of 0.02 S/cm, specific capacitance of 278 F/g at a current density of 1 A/g. The optimal MoS₂ QDs in DBC-PANI aerogel improves specific capacitance up to 796.2 F/g at 1 A/g with superior rate capability (582 F/g at 20 A/g), and long cycling stability (86% after 5000 cycles). Also, the hybrid conductive DBC-MoS₂-PANI aerogels thus produced act as an efficient electrocatalyst showing lower HER overpotential in comparison to MoS₂ sheets and MoS₂ QDs. It exhibits an optimum overpotential value of 196 mV at 10 mA cm⁻², a favorable Tafel slope of 58 mV/dec, and an excellent electrocatalytic stability. Here, porous aerogel facilitate the fast diffusion of electrons/ions in the electrode, which can achieve high energy supercapacitor and the HER catalysis.

1. S. Das et al., *ACS Appl. Mater. Interfaces* 8 (2016), 28055–28067.
2. X. Geng et al., *Adv. Funct. Mater.* 24 (2014), 6123–6129.

Formation of recognition sites in an acrylic polymer by the molecular printing technique

Ouahiba BELADGHAME¹, Nouria BOUCHIKHI², Djahida LERARI², Ulrich MASCHKE³,
Lamia BEDJAQUI-ALACHAHER¹

¹ *Laboratoire de Recherche sur les Macromolécules, Université de Tlemcen*

² *Centre de Recherche Scientifique et Technique en Analyses Physico-chimiques, Tipaza*

³ *Université des Sciences et Technologies de Lille 1*

email corresponding author: l_bedjaoui@mail.univ-tlemcen.dz

The technique of molecular Imprinting has undergone remarkable development over the last decades, this technology has increased tremendously in last years. The recognition capabilities of molecularly imprinted polymers (MIPs) are being successfully exploited in many application areas such as sensors, separations and extraction of chemical compounds, drug development, and drug delivery [1-3]. The work presented here focuses on the elaboration and the characterisation of MIPs by non-covalent approach in presence of a target molecule. The MIP materials were prepared by radical photo-polymerisation of mixture containing the *n*-butylacrylate (BuA) as monomer, 1,6-hexanedioldiacrylate (HDDA) as cross-linking agent and 2-hydroxy-2-methyl-1-phenyl-propane-1-one as photo-initiator. The printed molecule chosen is 2-phenoxy-propionic acid (APP) analogous to (2,4-D) herbicide. Non-imprinted materials (NIPs) and imprinted materials (MIPs) were characterized by infrared spectroscopy (FTIR), and differential scanning calorimetry (DSC). The Infra Red (IR) analysis confirmed the presence of non-covalent hydrogen bond between the target molecule and the monomer in pre-polymerisation mixture. The extraction of the target by several washes was confirmed by UV spectroscopy. The recognition properties of the NIP and MIP materials obtained toward APP were evaluated by gas chromatography analysis. The obtained results showed a specificity of printed materials.

1. G. Kerstin, I.A. Nicholls, *Europ. Polym. J.* 75 (2016), 423–430.
2. K. Puzio, R. Delépée, R. Vidal, L.A. Agrofoglio, *Anal. Chim. Acta.* 790 (2013), 47–55.
3. G. Vasapollo, R.D. Sole, L. Mergola et al., *Int. J. Mol. Sci.* 12 (2011), 5908–5945.

Experimental evidence of molecular relaxation processes in cellulose-amine physical complexes

Agustin RIOS DE ANDA^{1,3}, Laurent HEUX¹, Caroll VERGELATI², Karim MAZEAU¹, Yoshiharu NISHIYAMA¹

¹ CERMAV-CNRS, Grenoble

² Solvay RICL, Saint-Fons

³ Institut de Chimie et des Matériaux Paris Est, Thiais

email corresponding author: rios@icmpe.cnrs.fr

Cellulose complexes with a series of amines of various sizes and chemical structures were studied in this work. These complexes were obtained by putting microfibrillated cellulose films or Flax fibers in contact with a solution of ethylenediamine (EDA) and a target mono- or diamine under an inert atmosphere while raising the temperature. Excess of EDA could be eliminated under vacuum overnight while maintaining the complex with larger amines. Wide Angle X-ray Scattering (WAXS) characterization showed that amine intercalated in cellulose III-like structure with the d(010) spacing linearly increasing with the molar volume of the amine. Modulated Differential Scanning Calorimetry (MDSC), Dynamic Mechanical Analysis (DMA), and Broadband Dielectric Spectroscopy measurements showed the presence of two glass transition-like processes (T_g) in all studied complexes. The first transition occurred at ca. 0°C and its value is independent from the amine size. The second transition appeared at between 80 and 110°C and depends on the size of the amine, i.e. when the amine molecular size increases, the T_g decreases. Solid-state ¹³C NMR CP-MAS and 2D WISE measurements at increasing temperatures showed that, when approaching the second T_g, a fraction of the amine peaks became closer to the chemical displacements at liquid state. The fraction of such amine increased with temperature. Moreover NMR T₁ relaxation time measurements showed that the complexed amines possessed two to three relaxation domains and their corresponding relaxation times became shorter with increasing temperature. With these results we have attributed the first T_g to molecular motions of the complexed amines within the cellulose structure while the second high-temperature T_g would correspond to the molecular relaxation of the cellulose-amine complexes. Mechanical characterization of complexed films at various temperatures will be carried out to relate the complexes' mechanical properties with their molecular mobility.

Insights into cellulose solvation in organosolv mixtures: a molecular dynamics and quantum mechanics study

Sonia M. AGUILERA-SEGURA, Tzonka MINEVA, Francesco DI RENZO, Julie BOSSU

Institut Charles Gerhardt Montpellier

email corresponding author: sonia-milena.aguilera-segura@enscm.fr

The use of multicomponent solvents has provided remarkable results in biomass fractionation processes of several levels of severity. Despite all invested efforts, no fractionation method is currently capable of achieving lignocellulose deconstruction in an economically viable commercial scale process. Understanding the factors that drive to the interaction of biomass with different solvents is the key to successful fractionation. Understanding the mutual organization between organic solvents and water in multi-component systems and their specific interactions with the wood polymers can be achieved by means of computational methods, which can provide detailed information at the molecular level. Our results on the atomistic understanding of preferential interactions of water-organics solvent components with cellulose have been obtained from molecular dynamics simulations in conjunction with density functional theory (DFT) approaches, including ab-initio molecular dynamics. Structure and dynamics of cellulose-solvent interfaces were characterized by torsion angles of cellulose backbone and hydroxymethyl chains, H-bonding, interaction energies, and pair correlation functions (RDF) at several water-organosolv concentrations. Structure analysis shows that chain deformation of solvated cellulose by conformational transition of the hydroxymethyl chain evolves in the order water>ethanol> isopropanol>acetone. The center-of-mass RDFs revealed a saturation-like behavior of some concentrated mixtures, displaying a solvent phase separation at the cellulose interface. Furthermore, analysis of the site-to-site RDFs shows a preferential orientation of solvent molecules toward specific oxygens of the glucose monomer. This preferential solvent-O(cellulose) binding vary with the nature of the organic solvent and the water content. Non-linearity of interactions between mixed solvents and cellulose is in good agreement with experimental swelling data [1].

1. J. Bossu, N. Le Moigne, S. Corn et al., *Wood Sci. Technol.* 52 (2018), 987–1008.

Structure and molecular interactions of chitin crystallosolvates

Yu OGAWA

CERMAV-CNRS, Grenoble

email corresponding author: yu.ogawa@cermav.cnrs.fr

Chitin, the second most abundant biopolymer after cellulose, forms crystallosolvates with various small compounds such as water [1] and alcohols [2] as well as amines and organic acids [3]. Over the last decade, a number of high resolution structures of chitin and chitin crystallosolvates have been reported based on X-ray and neutron diffraction techniques [4,5]. Such high-resolution structures have served as a basis for theoretical studies on these crystals to elucidate their molecular interactions. Molecular modelling allows us to understand not only the static crystal structures but also the dynamics of guest molecules in the crystalline lattices [6]. In this contribution, an overview will be given on the crystal structures and molecular interactions in chitin crystallosolvates. The role of intermolecular hydrogen bonds as well as their dynamics will be further discussed based on molecular dynamics and density functional theory calculation studies.

1. J. Blackwell, *Biopolymers* 7 (1969), 281–298.
2. Y. Saito et al. in “*Advances in Chitin Science II*” (1998), pp. 507–512.
3. Y. Noishiki et al., *Macromolecules* 37 (2004), 6839–6842.
4. Y. Nishiyama et al., *Macromolecules* 44 (2011), 950–957.
5. D. Sawada et al., *PlosOne* (2012), e39376.
6. D. Sawada et al., *Cryst. Growth. Des.* 16 (2016) 3345–3352.

Adsorption of oligo-ampholytes to like-charged polyelectrolytes

Raju LUNKAD, Peter KOŠOVAN

Charles University, Prague

email corresponding author: peter.kosovan@natur.cuni.cz

Proteins are known to adsorb to polyelectrolytes on the “wrong” side of the isoelectric point, i.e. when the overall charge of the protein has the same sign as that of the polyelectrolyte. This has been attributed to patchy charge distribution on the proteins, whereas changes in their ionization upon adsorption have been neglected. In this work we show that the patchy charge distribution is not necessary if pH-responsive ionization of the charged groups is taken into account. We demonstrate it using a model system of a star-like anionic polyelectrolyte and an oligo-ampholyte, consisting of several acid (A) and base (B) groups. Using molecular dynamics simulations in the reaction ensemble show that the acid and base groups on a generic oligomer AAA-BBB adopt their ionization state to the local environment. Under suitable conditions, the negatively charged oligo-ampholyte in the bulk coexists with its positively charged form adsorbed on the polyanion. Our simulations thus put forward a new paradigm for the interpretation of protein-polyelectrolyte interactions, and demonstrate that the changes in protein ionization must be taken into account. Furthermore, it provides a guideline for the design of bio-inspired oligo-ampholytes which would adsorb to polyelectrolytes under desired conditions, determined by the ionization constants, pKa and pKb of the ampholytes.

Hyaluronic–pluronic mixed system: depletion interaction between micelles triggered by the polyelectrolyte chain conformation

Isabelle GRILLO¹, Jérôme COMBET², Isabelle MORFIN³

¹ *Institut Laue-Langevin, Grenoble*

² *Institut Charles Sadron, Strasbourg*

³ *Laboratoire Interdisciplinaire de Physique, Grenoble*

email corresponding author: grillo@ill.fr

In the medical field and especially for cancer treatment, intensive researches are performed to deliver the drug at the right position allowing to reduce the dose and side effects. The poor solubility in biological fluids of most of the approved drugs obliges to encapsulate them into carriers. The triblock copolymers Pluronics are bio-compatible and are stealth carriers [1]. Hyaluronic acid (HA) is a natural polyelectrolyte largely found in the body and currently investigated as a target-specific material because many malignant cancer cells overexpress HA receptors [2]. The aim of the study is to characterize the structure of HA–Pluronic (F127) assemblies as a function of different parameters such as concentration, ionic strength and temperature. Small angle neutron scattering experiment demonstrate that HA does not modify the size and shape of the individual micelles. In pure water, the spatial distribution of micelles is not affected by the polyelectrolyte. By increasing the ionic strength, the formation of small micellar clusters which crystallize into a fcc crystal liquid phase at high ionic strength is observed. This behavior is reinforced by increasing the HA concentration or the molecular weight of the chain. The nature of the salt plays also a role following the Hofmeister series and divalent cations such as Ca^{2++} have drastic effects on the micellar collapse. The origin of the behavior is the change of the HA chain conformation -from stretched to coil-by addition of salt which induces an excluded volume around the micelles. Consequently, the formation of micellar clusters and their collapse can be understood through a depletion mechanism.

1. M. Valero et al., *J. Phys. Chem. B* 116 (2012), 1273–1281.
2. U. Richter et al., *Histochem. Cell Biol.* 137 (2012), 687–695.

Efficient facilitated transport of lead and cadmium across a plasticized triacetate membrane mediated by organo-phosphorous carrier

Naima ABDELLAOUI, Omar AROUS, Rachida BOUMEHDI, Siham ABABSA

Faculté de Chimie, USTHB, Algiers

email corresponding author: naima.abdellaoui1973@gmail.com

This paper reports on the synthesis of a novel class of polymer inclusion membranes prepared by thermally induced phase separation using a mixture of two polymers: polyvinylidene fluoride (PVDF) and cellulose triacetate (CTA) plasticized by dioctylphthalate (DOP) doped with organo-phosphoric compound: trioctyl phosphine oxide noted (TOPO) as mobile carrier. The membranes polymers-plasticizer-carrier were characterized using chemical techniques as well as Fourier Transform Infra-Red (FTIR), X-ray Diffraction (XRD), and Thermogravimetric Analysis (TGA). All synthesized polymeric membranes are applied for investigation to the facilitated transport of Pb(II) and Cd(II) ions from aqueous nitrate source phase. The PVDF and PVDF + CTA membranes presented a homogeneous and dense structure while the PVDF + CTA + DOP and PVDF + CTA + DOP + TOPO membranes obtained a well distributed porous structure. All membranes were thermally stable up to nearly 200°C A study of the transport across a polymer inclusion membrane has shown that the lead or cadmium transport efficiency was increased using TOPO as carrier at pH 6-7. This study represents an interesting approach in the treatment of hydrometallurgical solutions using the TOPO neutral carrier mediated transport.

Opportunities and challenges for small-angle neutron scattering of polymers

Sylvain PREVOST

Institut Laue-Langevin, Grenoble

email corresponding author: prevost@ill.fr

For the past 5 decades, small angle scattering techniques have brought considerable knowledge on polymers (melt, blends, in solution, self-assembling), and the isotopic labelling allowed by neutrons has been leveraged to offer a unique insight. With modern sources and instruments, the flux, data quality and window of observation that span from atoms to micrometers is creating new possibilities of investigations, but also demonstrating sometimes the limits of our current understanding of polymers, whether at the short scale of monomers and solvent molecules or at the long scale where chain-chain interactions occur even in dilute conditions. These problems are illustrative of the challenges in multi-scale simulations that must be tackled to mine the whole information content of experimental data sets. We will show developments of instruments, sample-environment and data handling but also examples of actual data that defy our analysis.

POSTER ABSTRACTS

P1. The effect of crown-ethers additives on poly(2-[N,N diethylaminoethyl] methacrylate) (PDAEM) and cellulose triacetate (CTA) a symmetric dialysis membrane performance

Naima ABDELLAOUI, Zahra HIMEUR, Omar AROUS

Faculté de Chimie, USTHB, Algiers

email corresponding author: omararous@yahoo.fr

Polymer inclusion membranes used for selective transport and separation of metallic ions has emerged in recent times. Their expansion depends on the method of preparation and the study of their structure. In this paper, an improvement of a novel category of thin films for performing ions separation was reported. The membrane was elaborated using a mixture of polymers: cellulose triacetate (CTA) and 2-[N,N diethylaminoethyl] (PDAEM) and plasticized by 2-Nitrophenyl pentyl-ether (NPPE) and crown ethers incorporated into the polymer as a metal ion carrier. The membranes (polymer1–plasticizer–polymer2) were synthesized using a new method and characterized by various techniques including Fourier Transform Infrared (FTIR) spectroscopy, X-Ray Diffraction (XRD), Thermogravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM). The CTA membrane exhibited by well-defined pores completely filled with the second polymer and plasticizer (NPPE). Surfaces of all synthesized membranes were found to be smooth. The systems constituted by the mixture of (polymer1 + plasticizer + polymer2 + carrier) did not give any diffraction. This could be due to the absence of crystallization within the membrane. Overall, our results showed that the addition of plasticizer with two polymers resulted in homogeneous and hydrophobic membranes whose physical properties, such as density, thickness, and hydrophobicity, were modified. As applications, transport of Pb(II) in polymeric membranes (PIM) was studied.

P2. Photo-electrodialysis combination system for Pb²⁺ removal using polymeric membrane/semiconductor

Akkacha MAZARI¹, Mouhamed TRARI¹, Omar AROUS²

¹ *Laboratory of Storage and Valorization of Renewable Energies, USTHB, Algiers*

² *Faculté de Chimie, USTHB, Algiers*

email corresponding author: chimi24@hotmail.fr

The present work combines the solar energy with the environmental protection through the membrane selectivity for metallic ions. Firstly, we have elaborated new polymeric membranes for ions separation. The membrane is polymerized from cellulose triacetate modified by poly-ethyleneimine and plasticized by 2-nitrophenyl pentyl ether. Different membranes are characterized by Fourier Transform Infra-Red (FTIR), X-Ray Diffraction (XRD), Thermo-Gravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM). In a second part, we have prepared two new photo-electrodes, crystallizing in the brownmillerite structure: n-Sr₂Fe₂O₅ and p-CuCrO₂ and their photo-electrochemical characterizations are undertaken. The photo-electrodialysis indicates that the combined system pCuCrO₂/membrane/n-Sr₂Fe₂O₅ enhances considerably the electron transfer and the diffusion flux of Pb²⁺. The diffusion flux of cadmium increases considerably when the electrode is exposed to visible light. The results show that the transport percentages of Cd²⁺ increases by 86% under solar energy and 35% using a tungsten lamp.

P3. Effect of crosslinking agent and nature of solvent on the swelling behavior of pIBOA-co-2-EHA

Dounya MERAH¹, Ulrich MASCHKE², Lamia BEDJAOUI-ALACHAHER¹

¹ *Laboratoire de Recherche sur les Macromolécules, Université de Tlemcen*

² *Université des Sciences et Technologies de Lille 1*

email corresponding author: l_bedjaoui@mail.univ-tlemcen.dz

Copolymers are widely employed in industrial processes because their physico-chemical properties, like strength, elasticity or thermal behaviour, can be modified by varying their macromolecular composition. Poly isobornyl acrylate (PIBOA) is a commercial available polymer with many attractive, industrial qualities, including excellent transparency, low refractive index, low thermal expansion, high weather resistance, and low birefringence [1,2]. In this work, we are interested in the development of a copolymer based on two acrylic monomers: Isobornyl Acrylate (IBOA) and 2-Ethylhexyl Acrylate (2-EHA). For this purpose we have prepared networks containing 60 wt.% of IBOA and 40 wt.% of 2-EHA using two different crosslinking agents: hexane-1,6-diol-diacrylate (HDDA) and acrylic acid 6-(4)-(6-acryloyloxy-hexyloxy) biphenyl-4-yloxy) hexyl ester (AHBH) and as a photoinitiator: 2-Hydroxy-2-methyl-1-phenyl-propan-1-one (Darocur). The mixtures obtained were irradiated under UV ($\lambda = 365$ nm). The polymerization was followed by Fourier Transform Infrared (FTIR) spectrophotometry, showing rapid kinetics in the presence of EHA. Then all the networks were characterized by the differential scanning calorimetry (DSC) [3,4] to determine the glass transition temperature (T_g) for the two copolymers. The swelling was studied by polarized light optical microscopy (POM) for the IBOA/EHA/HDDA copolymer, using organic solvents such as toluene and 1-heptanol. In addition the swelling study of IBOA/EHA/AHBH was investigated in nematic solvent 4-cyano-4'-n-pentylbiphenyl (5CB).

1. W. Hu, H. Guo, Y. Chen, R. Xie, H. Jiang, P. He, *Eur. Polym. J.* 85 (2016), 313.
2. M. Mohammadi, H. Fazli, M. Karevan, J. Davoodi, *Eur. Polym. J.* 91 (2017), 121.
3. J. Qu, J. Cheng, Z. Wang, X. Han, M. Zhao, *Optical Mater.* 36 (2014), 804-808.
4. K. Urayama, Y.O. Arai, T. Takigawa, *Macromolecules* 38 (2005), 5721-5728.

P4. pH-responsive interpenetrating polymeric network based on cellulose/ poly(HEMA): elaboration and swelling behavior

Meriem MIHOUB¹, Ulrich MASCHKE², Lamia BEDJAOUI-ALACHAHER¹, Salah HAMRI³,
Tewfik BOUCHAOUR¹

¹ *Laboratoire de Recherche sur les Macromolécules, Université de Tlemcen*

² *Université des Sciences et Technologies de Lille 1*

³ *Centre de Recherche Scientifique et Technique en Analyses Physico-Chimiques, Tipaza*

email corresponding author: meriem.07m@hotmail.fr

pH-sensitive interpenetrating polymer network (IPN) is a class of materials widely used in water purification and drug delivery. This study shows the elaboration of such material based on both crosslinked cellulose and poly-hydroxyl-ethyl-methacrylate (poly-HEMA) through the sequenced synthesis method. Cellulose was crosslinked by epichlorohydrin whereas the poly-hydroxy-ethyl-methacrylate is polymerized under UV radiations, with hydroxyl-dioldi-acrylate (HDDA) as crosslinker. The FTIR spectroscopy confirms the formation of the new physically combined material (IPN). The characterization of these IPN by swelling study as a function of two parameters (pH and poly-HEMA rate) was investigated. In the first one, when pH values were varied at room temperature, we obtained a high swelling in basic pH and a slight difference between swelling in neutral and acidic pH medium, as well as a visible morphological change was observed. In the second one, by variation of the HEMA% in the composition of IPN, the experimental results shows that the swelling behavior is inversely proportional to the HEMA rate. The architecture of the IPN depend also to the epichlorhydrine rate within the cellulose gel.

P5. Effect of several parameters on the kinetic of polymerization of hydroxyethylacrylate (HEA) induced by visible light

Nouria BOUCHIKHI¹, Salah HAMRI¹, Djahida LERARI¹, Ulrich MASCHKE², Fayçal DERGAL¹, Khaldoun BACHARI¹, Lamia BEDJAOUI-ALACHAHER³,

¹ *Centre de Recherche Scientifique et Technique en Analyses Physico-Chimiques, Tipaza*

² *Université des Sciences et Technologies de Lille*

³ *Laboratoire de Recherche sur les Macromolécules, Université de Tlemcen*

email corresponding author: noura.bouchikhi@yahoo.fr

Radiation curing technologies provide a number of economic advantages over the usual thermal operation like: rapid through cure, low energy requirements, room temperature treatment, non-polluting, solvent-free formulations and low costs [1]. One of its applications is the light induced polymerization which has attracted great interest. Most research work into visible light-initiated photo-polymerization has focused on free-radical systems based primarily upon acrylates and methacrylates. For these systems, the activated photoinitiators are usually formed by two components as, for example, a dye and an amine [2]. Recently, the interest in the phenothiazinium dyes as photosensitizer of vinylic polymerization [3,4], has significantly increased due to their visible-light absorptivity. Among them ; the methylene blue (MB) which is a phenothiazinium compound that presents a planar heterocyclic aromatic structure, being characterized spectroscopically by an intense electronic absorption band in the red spectral region (~664 nm). The photo-polymerizable system used in this contribution is based on hydroxy ethyl acrylate monomer, noted HEA using the methylene blue (MB) as a sensitizer dye and an amine as co-initiator. The parameters effects on the polymerization kinetic were experimentally investigated such as dye and co-initiators concentrations, pH of the solution and the light intensity. The polymerization kinetic under visible light was studied using quantitative Fourier Transform Infrared spectroscopy (FTIR). Interestingly, the structure of the obtained material is considerably depended on these experimental parameters and a very high final conversion of monomers can be reached.

1. W.G. Santos et al., *J. Photochem. Photobiol. A Chem.* 252 (2013), 124-130.
2. D. Chelminiak, M. Ziegler-Borowska, H. Kaczmarek, *Mater. Lett.* 164 (2016), 464-467.
3. M.A. Tehfe, J. Lalevee et al., *Macromolecules* 42 (2009), 8669-8674.
4. M. Ortiz, A. Fragozo et al., *J. Photochem. Photobiol. A Chem.* 218 (2011), 26-32.

P6. Self-assembly of block copolymers of two negatively charged polyelectrolytes and multivalent cations

Nico CARL¹, Klaus HUBER², Ralf SCHWEINS¹, Sylvain PREVOST¹

¹ *Institut Laue-Langevin, Grenoble*

² *University of Paderborn*

email corresponding author: carlno@ill.fr

Polyelectrolytes are widely used in industrial processes as anti-scaling agents, for waste water treatment or as rheology modifier in cement. They also serve as model system for natural polyelectrolytes such as proteins. The specific interaction of the charged polymer chain with oppositely charged species such as surfactants or ions is the basis for many applications in household and industry. Previous works on two different negatively charged polyelectrolytes showed that the interaction with multivalent cations such as Ca^{2+} , Sr^{2+} or Ba^{2+} strongly depends on the chemical nature of the anionic moiety [1,2]. In the case of polyacrylic acid (PAA) phase separation occurs with Ca^{2+} , Sr^{2+} and Ba^{2+} , whereas polystyrene sulfonate (PSS) only shows a phase separation with Ba^{2+} . We use this cation selectivity to self-assemble a block copolymer (PAA-*b*-PSS) consisting of polyacrylic acid and polystyrene sulfonate into well-defined micelles. The structure of these micelles was studied by a combination of light, small-angle neutron and X-ray scattering. Internal and external contrast variation in SANS by using different $\text{H}_2\text{O}/\text{D}_2\text{O}$ ratios as well as partly deuterated polymers provides detailed information about the polymer structure. On the other hand, SAXS gives information about the location of the multivalent cations. The block copolymer micelles show multi-responsive behavior towards pH, temperature or salt concentration. The present work demonstrates that the system can be switched between lower (LCST) and upper critical solution temperature (UCST) by changing from Ca^{2+} to Ba^{2+} . By using Sr^{2+} as a counter ion, we were able to combine LCST and UCST behaviour and create a double thermoresponsive system. Isothermal titration calorimetry complements our scattering data and shows that the temperature behaviour is a subtle balance between the release of counter ions and binding enthalpy. Understanding these interactions allows us to design new responsive and schizophrenic materials.

1. M. Hansch et al., *J. Chem. Phys.* (2018), 114906.
2. S. Lages et al., *Macromolecules* 42 (2009), 4288-4299.

P7. Structural investigation of biopolyelectrolyte-surfactant complexes: Developments in the understanding of viscosity behaviour

Giuseppe Rosario DEL SORBO¹, Ingo HOFFMANN², Emanuel SCHNECK¹

¹ *Max Planck Institute of Colloids and Interfaces, Potsdam*

² *Institut Laue-Langevin, Grenoble*

email corresponding author: del-sorbo@ill.fr

Oppositely charged polyelectrolyte (PE)-Surfactant Complexes (OP-SCs) have attracted much interest over the past decades. Not last because of their relevance in numerous household applications such as detergency and paints, or as rheological modifiers [1]. In general, these mixtures form clear, homogeneous solutions if either an excess of PE or surfactant charges is present and precipitates around charge equilibrium. Near the phase boundary on the PE-rich side, depending on their composition and chemical nature, some of these OPSCs can greatly increase the viscosity of aqueous solutions upon addition of relatively small amounts of material on the order of less than 1 wt%, while others have no effect [2]. The behaviour of the system is governed by a number of parameters, including the composition, the chemical nature of the PE and the surfactant. Here, we have investigated OPSCs consisting of the well-characterised PE JR 400 and two different surfactants, namely sodiumoctyl sulphate (SOS) and sodium tetradecyl sulphate (STS), which only differ in the length of their alkyl chains. In a preliminary study, the system's phase behaviour and viscosity have been investigated, showing that the viscosity of JR 400/STS is significantly increased near the phase boundary, while SOS did not show a significant effect in tube inversion tests. Therefore, we can assume that the surfactant chain length plays a crucial role for the rheological behaviour of OPSCs. In order to achieve this information, different kind of experiments were performed such as Dynamic Light Scattering and Small Angle Neutron Scattering measurements.

1. E.D. Goddard, R.B. Hannan, *J. Colloid Interface Sci.* 55 (1976), 73-79.
2. I. Hoffmann, B. Farago et al., *J. Chem. Phys.* 143 (2015), 1-11.

P9. Development of active films based on poly(butylene adipate-co-terephthalate) filled with silver-montmorillonite nanoparticles for food packaging use

Assia Siham HADJ-HAMOU, Manel SERAY, Fayçal BENHACINE

Laboratoire des Matériaux Polymères, USTHB

email corresponding author: hadjhamouassia@yahoo.fr

Active films made of poly (butylene adipate-co-terephthalate) and a small amount of silver exchanged montmorillonite (2, 3 and 5% by weight) for food packaging use were successfully prepared via solvent casting method. PBAT/AgMMT nanocomposites containing different AgMMT loadings were characterized by several techniques. X-Ray Diffraction, UV-visible Spectroscopy and Transmission Electron Microscopy results revealed the formation of exfoliated nanocomposites structures with a random dispersion of spherical Ag nanoparticles. These nanocomposites films have showed an interesting improvement in their barrier properties and a strong antibacterial efficiency against *S. aureus* and *E. coli* bacteria. The potential of the silver ion release from the PBAT/AgMMT films to a slightly acidified aqueous medium was measured by Atomic Absorption Spectroscopy. The results exhibited a gradual increase of the amount of silver ions released up to 30 days of immersion. The kinetic study of the ions release showed that the release's mechanism is governed by the diffusion process.

P10. Deuteration of biomolecules for neutron scattering studies

Michael HÄRTLEIN, Martine MOULIN, Juliette DEVOS, Valérie LAUX, Trevor FORSYTH

Institut Laue-Langevin, Grenoble

email corresponding author: haertlein@ill.fr

Neutron scattering studies offer unique insights to biopolymers. This results mainly from the fact that the scattering power for neutrons of hydrogen is comparable to the other atoms typically found in biological macromolecules, contrasting strongly with the situation for X-rays where hydrogen atoms scatter very weakly. This is of crucial importance given that about half of the atoms in biological molecules are hydrogen and that they are often highly significant to biological structure and function. Deuteration, the replacement of hydrogen atoms by the stable isotope deuterium is a powerful method for the investigation of the structure and dynamics of biomolecules by means of neutron scattering. The pronounced differences in the scattering cross sections between hydrogen- and deuterium containing molecules allows to highlight parts of molecular complexes by neutron scattering methods such as small-angle neutron scattering or neutron reflectometry. In neutron crystallography perdeuteration allows the work with smaller crystals and facilitates the interpretation of nuclear density maps. The Institut Laue-Langevin Life Sciences Group operates a Deuteration Laboratory (D-Lab) as a platform within the *Partnership for Structural Biology*. Protocols for the complete, partial or selective *in vivo* deuteration of biomolecules have been developed. Generally, *Escherichia coli* or *Pichia pastoris* high cell-density fermenter cultures are used for the deuteration of recombinantly expressed proteins, nucleic acids and lipids such as phosphatidylcholine or cholesterol. Deuterated biomolecules produced in the ILL D-lab were essential for recently published neutron scattering work in high impact journals.

Access to the ILL / PSB Deuteration platform is via a peer review procedure, details of which can be found at: <http://www.ill.fr/deuteration>.

P11. Transparent moisture barrier using surface-modified nanoclay composite for OLED encapsulation

Hyeon-Gyun IM, Dong Jun KANG

Korea Electrotechnology Research Institute

email corresponding author: hgim@keri.re.kr

We report the facile fabrication of transparent and high-performance moisture barrier material (SC nanocomposite) using surface-modified bentonite clay (SC) as nanofiller and glycidyl silane as a surface-modifier/binder via simple, cost-effective and mass-producible process. SC is synthesised using a base-catalysed sol-gel process; their hydroxyl surfaces are decorated with glycidyl ligands to endure the densely stacked structure and high clay content in the final nanocomposite. The SC nanocomposite barrier exhibits high optical transparency (> 90), dense multi-stacked clay structure, and considerably enhanced moisture barrier performance. We discuss the fabrication and physical properties of the SC nanocomposite. To assess the applicability of the nanocomposite as a high-performance barrier material in practical applications, typical organic light-emitting devices are encapsulated, and their lifetime is evaluated.

P12. Robust transparent protective hard-coating using physicochemically-incorporated silica nanoparticles and organosiloxanes

Hyeon-Gyun IM, Dong Jun KANG

Korea Electrotechnology Research Institute

email corresponding author: kangdj@keri.re.kr

We report on the synthesis of a silica nanoparticle (NP)-reinforced oligosiloxane nanohybrid material (SM-nanocomposite) and demonstrate its properties as a robust transparent hard coating material for various applications. The oligosiloxane (MMO) resin as a matrix was synthesized using methyl and methacryl silanes via a hydrolytic sol-gel condensation. The silica NPs with various sizes (12, 20 and 60 nm) as nanofillers were also synthesized through a hydrolytic sol-gel condensation, and the surface of NPs was organically modified with methyl and methacryl functions, which allowed stable dispersion and chemical cross-linking of the NPs with MMO matrix. In this work, we introduce synthetic steps of the nanocomposite and discuss the optical, morphological, thermal and mechanical properties of the composite.

P13. Crystal structure of V-amylose inclusion complexes: new developments and some surprises

Cong-Anh-Khanh LE¹, Yu OGAWA¹, Luc CHOISNARD², Denis WOUESSIDJEWE², Jean-Luc PUTAUX¹

¹ CERMAV-CNRS, Grenoble

² DPM, Univ. Grenoble Alpes, CNRS, Grenoble

email corresponding author: le@cermav.cnrs.fr

Amylose forms crystalline inclusion compounds with a large variety of small molecules (alcohols, fatty acids, aroma compounds, etc.). In these crystallosolvates, the so-called "V-amylose" occurs as single helices and the ligands can be located inside the helices, in-between or both. Previous exploratory studies of V-amylose polymorphism like those by Takeo and Kuge [1] or Yamashita and coll. [2] in the 60-70's, and Chanzy's group [3] in the 80-90's have produced several tentative molecular models based on 6-, 7- and 8-fold single helices. However, only a small number of structures have been characterized by crystallographic methods. By analyzing model lamellar crystals prepared from dilute aqueous amylose solutions by a combination of TEM imaging and electron and X-ray diffraction, our results show that polymorphism is a more general behavior than previously known. Depending on the crystallization conditions (crystallization temperature, concentration of complexing agents, solvent composition), a number of ligands induced the formation of distinct allomorphs. Moreover, several new allomorphs prepared with specific ligands have been identified. Some allomorphs exhibited nearly identical morphologies and were only distinguished by diffraction techniques. ¹³C CP/MAS NMR data also confirmed that the chemical shift of the carbon C1 of the glucose unit would be a good indicator of the amylose helical conformation (6-, 7- or 8-fold). In view of these results, it is likely that new crystal forms of V-amylose still remain to be discovered.

We thank LabEx Arcane (Grenoble) for the financial support of C.A.K. Le's PhD, and the ICMG-NanoBio platform (Grenoble) for granting access to the Electron Microscopy facility.

1. K.-I. Takeo, T. Kuge, *Agric. Biol. Chem.* 33 (1969), 1174-1180.
2. Y.-H. Yamashita, J. Ryugo, K. Monobe, *J. Electron Microsc.* 22 (1973), 19-26.
3. W. Helbert, "*Données sur la structure du grain d'amidon et des produits de recristallisation de l'amylose*", Doctoral dissertation, Université de Grenoble 1, 1994.

P14. Miscibility, thermal stability and non-isothermal decomposition kinetic of polymer blends based on poly(vinylchloride) and poly(methylmethacrylate-co-4-vinylpyridine)

Farid METREF, Abderahmane OUARGLI, Samia CHEKROUN

Laboratoire des Matériaux Polymères, USTHB, Algiers

email corresponding author: fmetref2000@yahoo.fr

To develop new polymer materials with new properties, polymer mixtures are one of the most used methods. A mixture of two polymers may lead either to interpolymer complex or to a blend. The temperature, the solvent and the hydrophobicity of the polymers are among the most important factors that influence the formation and stability of such polymer mixtures. Proton donor poly (vinyl chloride) (PVC) and proton-acceptor poly (methyl methacrylate-co-4-vinylpyridine) (MM4VP-x) copolymers (x% is amount of 4-vinylpyridine) was prepared by free radical polymerization and characterized. Due to the acidic hydrogen atom of PVC and 4-vinylpyridine specific interactions that occurred up on mixing pairs of these polymers, a soluble or precipitate interpolymer complexes or blends, can be obtained in THF and butan-2-one. Preliminary tests of miscibility and complexation of PVC/MM4VP-x mixtures were performed in THF. A viscometry study confirms the obtaining one (soluble complex) of the two types of interpolymer complexes from the behavior of the reduced viscosity of their blend solutions with blend composition. The FTIR spectra of PVC/MM4VP-x blends in the 1620-1580 cm⁻¹ region confirms the presence of the peak at 1606 cm⁻¹ of specific interactions. The glass temperature transition T_g of all mixtures of the system PVC/MM4VP-31 were determined using the differential scanning calorimetry (DSC). This latter reveals the existence of a single T_g in the whole area of the composition. Theoretical Kwei and Brostow approaches were used to describe the T_g-composition behaviours. A thermal stability study of PVC/MM4VP-x mixtures using TGA was performed. The kinetic method Tang et al. [1] was applied to study the degradation kinetic of materials. The activation energies, the degradation kinetic models, the pre-exponential factors of the PVC, MM4VP-x and those of their blends were determined.

1. W. Tang, Y. Liu, H. Zhang, C. Wang, *Thermochimica Acta* 408 (2003), 39-43.

P15. Hydration of hyaluronan in electrostatic self-assemblies

Isabelle MORFIN¹, Jérôme COMBET², Sylvie SPAGNOLI¹, Marie PLAZANET¹, Judith PETERS¹

¹ *Laboratoire Interdisciplinaire de Physique, Grenoble*

² *Institut Charles Sadron, Strasbourg*

email corresponding author: isabelle.morfin@univ-grenoble-alpes.fr

Hyaluronic acid (HA) is one of the most important polysaccharide in biology. It is often associated with proteins (or other molecules) by specific interactions, but also via electrostatic interactions, hydrogen bonding and hydrophobic forces. One important property of HA is that its biological function can be various depending on its molecular weight and like any biological system, its functionality is related to the dynamics of hydration water [1]. We investigated the hydration water dynamics around HA molecules of distinct molecular masses in pure water as well as in their complexes with oppositely charged surfactants (dodecyltrimethylammonium bromide, DTAB) by the means of elastic incoherent neutron scattering. With the aim of understanding the role of water molecules surrounding HA chains in the mechanisms of associations, in particular as function of the chain length of HA, we performed elastic neutron scattering on the IN13 CRG beamline at the Institut Laue-Langevin, France. From the pico- to the nanosecond time scale, IN13 gives access to the dynamics of water molecules on one side, and to polymer or larger molecule dynamics on the other side.

1. J.M. Cyphert, C.S. Trempus, S. Garantziotis, *Int. J. Cell Biol.* 2015 (2015), 563818.

P16. Effect of chain length alteration on the self-assembly of poly(ϵ -caprolactone) functionalized graphene quantum dots

Arun K. NANDI¹, Nabasmita MAITY¹

¹ *Indian Association for the Cultivation of Science, Kolkata*

email corresponding author: nabasmitamaity.89@gmail.com

In spite of their multifarious applications, graphene quantum dots (GQDs) necessitate surface modifications to enhance their solution processability. To alleviate the problem, we have synthesized four poly(ϵ -caprolactone) (PCL) functionalized GQDs (S1-S4) with different degrees of polymerization (3, 7, 15 and 21) of PCL using ring opening polymerization. The as synthesized materials show self-assembly behavior in chloroform producing green emitting gels. Optical and morphological studies unveil the transformation of the assemblies from J-aggregates to H-aggregates, accompanied by alteration in morphology from toroid (S1) to spheroid (S2) to rod like (S3, S4) structures, with increase in chain length of PCL. Functionalized GQDs with lower chain lengths of PCL (S1 and S2) also assembles into liquid crystalline phases as observed from birefringent textures under a polarized optical microscope, which is later correlated to the formation of columnar hexagonal (Colh) mesophases. However, no such behavior is observed at higher chain lengths of PCL under identical conditions. So, it is obvious that variation of PCL chain length plays a crucial role in the self-assembly, which is primarily triggered by the van der Waals force acting between the polymer chains which dictates the π -stacking of GQDs, resulting in different self-aggregated behavior.

P17. Nanocomposite aerogels for removing water organic pollutants

Wanda NAVARRA¹, Olga SACCO², Vincenzo VAIANO², Vincenzo VENDITTO¹, Christophe DANIEL¹

¹ *Department of Chemistry and Biology A. Zambelli, University of Salerno*

² *Department of Industrial Engineering, University of Salerno*

email corresponding author: wnavarra@unisa.it

At present, the water pollution is the most important problem for the environment sustainability. Among the contaminants that cause the greatest concern, there are the Contaminants of Emerging Concern (CECs). These compounds are PCBs, pesticides, herbicides, phenols, polycyclic aromatic hydrocarbons (PAHs), Persistent Organic Pollutants (POPs) and Pharmaceuticals and Personal Care Products (PPCP). To remove these pollutants from wastewater conventional physical and biological wastewater treatment are used. Unfortunately, these treatments can only partially remove CECs, without degrading them. Heterogeneous photocatalysis, instead, could be used to degrade organic pollutants to simpler compounds or totally mineralize them [1]. Photocatalyst, in form of nanopowder or nanocomposite, is generally dispersed in a slurry reactor as suspended powder. Moreover, the use of photocatalyst nanopowder has some drawbacks, it increases the costs of powder separation from purified water and damages the reactor recirculation pump. A possible solution could be to fix the catalyst on supporting organic or inorganic materials [2]. To fix the powder, highly porous monolithic aerogels, which are easily obtained by drying physical gels with supercritical CO₂, are very attractive materials. Physically crosslinked aerogels are obtained with different thermoplastic polymers such as polyethylene, syndiotactic polystyrene (s-PS), poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), poly(ether-ether-ketone) or poly(lactic acid). Crosslinked aerogels with peculiar nanoporous crystalline structures are obtained by using PPO and s-PS. It is known that these systems absorb volatile organic compounds (VOCs), halogenated or aromatic hydrocarbons, from water and air, also when present at very low concentrations [3]. In this contribution, the photocatalytic activity of different nanocomposites catalyst/aerogel based on N-doped TiO₂ and ZnO as catalysts and s-PS as polymeric matrix, in the degradation of target pollutants is reported and compared with that of the catalysts in powder form.

1. B.D. Miklos et al., *Water Research* 139 (2018), 118-131.
2. C. Daniel et al., *Macromol. Rapid Commun.* 34 (2013), 1194-1207.
3. C. Daniel, D. Sannino, G. Guerra, *Chem. Mater.* 20 (2008), 577-582.

P18. Morphology and thermal behavior of blends and nanoblends based on poly(styrene-co-allyl alcohol)/cellulose acetate butyrate and an organically modified Maghnia bentonite

Kamal OUAAD¹, Said DJADOUN², Chihab MEHAÏ²

¹ *Laboratoire des Matériaux Polymères, USTHB, Bab Ezzouar*

² *Département de Chimie, Université M'Hamed Bougara, Boumerdes*

email corresponding author: ouakamel@yahoo.fr

Blends and nanoblends based on an organically modified bentonite, from Maghnia, Algeria, (OBT)(1.5 and 3 wt%) and poly (styrene-co-allyl alcohol) (PSAA) containing 40 mol% of allyl alcohol and of Cellulose Acetate Butyrate (CAB), were elaborated via solution intercalation method and characterized by several techniques such as Fourier transform infrared spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). The miscibility of these blends was studied by Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry DSC. Thermal analyses (TGA) confirmed a significant improvement of thermal stability of these nanocomposites compared to the virgin blend.

P19. Morphology and thermal stability of cellulose acetate butyrate and poly(ethylmethacrylate) nanoblends

Souad KADI², Kamal OUAAD¹, Said DJADOUN²

¹ *Laboratoire des Matériaux Polymères, USTHB, Bab Ezzouar*

² *Département de Chimie, Université M'Hamed Bougara, Boumerdes*

email corresponding author: ouakamel@yahoo.fr

Enhancing miscibility, mechanical and thermal properties of polymer blends by adding a nanofiller has received increasing attention in both scientific and industrial communities. Ternary nanoblends (PEMA/CAB/OMMT) based on cellulose acetate butyrate/ poly(ethyl methacrylate) blends, of different ratios (30/70, 50/50 and 70/30), and an organically modified bentonite (OMMT) (1, 2 and 4%) were prepared by solution method. The PEMA/CAB/OMMT samples were characterized by transmission electronic microscopy (TEM), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). These nanoblends were elaborated for the purpose of studying the effect of OMMT on the morphology and thermal behavior of PEMA/CAB blends. In order to have more information on the morphology of the nanoblends at the nanometric scale, a study was carried out by TEM. The PEMA/CAB/OMMT 1% and PEMA/CAB/OMMT 4% were analyzed at different level of magnifications. According to the TEM micrographs, a better dispersion of the OMMT is observed with the nanoblend (70/30/1%) compared to the system with 4% of OMMT. TEM micrographs highlight the formation of nanomaterial of intercalated and intercalated/partially exfoliated structures. The single T_g observed with the PEMA/CAB blends and their nanoblends is an evidence of their miscibility. Moreover, the presence of the OMMT in the PEMA/CAB matrix has a positive influence on their thermal stability. Thermograms of PEMA/CAB/OMMT systems show a better thermal stability than the virgin blend.

P20. Influence of temperature and concentration on the solution phase behavior of poly(N-isopropylacrylamide) homopolymers

Kristina WAGNER¹, Sylvain PREVOST², Nico CARL², Matthias KARG¹

¹ *Heinrich-Heine-University, Duesseldorf*

² *Institut Laue-Langevin, Grenoble*

email corresponding author: prevost@ill.fr

Poly(N-isopropylacrylamide) (PNIPAM) is a well-known thermoresponsive polymer showing a lower critical solution temperature (LCST) of approximately 32°C in water. Below the LCST, PNIPAM is commonly believed to be well-hydrated with a Gaussian coil conformation. Above the LCST polymer-water interactions become unfavorable leading to the release of water and the well-known coil-to-globule transition. In this contribution we present a study on the solution phase behavior of PNIPAM homopolymers in different solvents as a function of external parameters. For this we synthesized PNIPAM homopolymers by RAFT-polymerization resulting in α -dodecyltrithiocarbonate ω -carboxyl-terminated chains with different numbers of repetition units ranging from 80 to 250. We investigated the phase behavior of these homopolymers in water using dynamic light scattering (DLS) and small angle neutron scattering (SANS). Below the LCST, both methods revealed structures that do not correspond to Gaussian coils of single chains. The latter are only observed in tetrahydrofuran as dispersion medium. To get more insights into the interaction of the chains and structures we performed a detailed study of the phase behavior in dependence on the degree of polymerization, end group, concentration and temperature by SANS.

P21. Self-assembly of dendrimers and oppositely charged dyes as a function of solvent pH and salt content

Ralf SCHWEINS, Franziska GROEHN, Giacomo MARIANI

Institut Laue-Langevin, Grenoble

email corresponding author: schweins@ill.eu

Self-assembly is a widely occurring phenomenon in nature. Understanding the shape-determining factors is key for tailoring nanoparticles with desired structural properties. Furthermore, switchability between disassembled and the assembled state through external triggers would increase the application potential. This contribution will discuss nanoparticles consisting of positively charged polyelectrolytes and oppositely charged multivalent organic dye molecules. The main focus will be put on polyamidoamine (PAMAM) dendrimers as polyelectrolyte. Depending on the dendrimer generation and the valency of the employed dye molecule a vast variety of either elongated shapes or spherical shapes, both also as core-shell particles, can be generated. pH triggers the assembly process as at high pH the PAMAM is neutral and thus not forming complexes with the dye molecules. The nanoparticles were characterized using static and dynamic light scattering (SLS & DLS) as well as small-angle neutron scattering (SANS). The results were complemented by UV-Vis spectroscopy and isothermal titration calorimetry (ITC). Gathering all the information from structural characterization and thermodynamics allows to elucidate the self-assembly process and consequently to predict the shape of nanoparticles formed. A general combination of interactions like electrostatics, counterion release and geometric constraints governs the self-assembly process rather than one specific binding motif. UV light may also serve as a trigger to change the size and shape of self-assembled nanoparticles, as illustrated by an example using a linear cationic polyelectrolyte together with anisomerizable dye molecule.

List of participants

<p>AGUILERA SEGURA Sonia M. Ecole Nationale Supérieure de Chimie de Montpellier 104 rue de la Galera, 34090 Montpellier sonia-milena.aguilera-segura@enscm.fr</p>	<p>AROUS Omar Faculté de Chimie, USTHB, BP 32 El-Alia, 16111 Bab-Ezzouar, Algeria omararous@yahoo.fr</p>
<p>AUZELY Rachel Centre de Recherches sur Les Macromolécules Végétales CS40700, 38041 Grenoble cedex 9, France rachel.auzely@cermav.cnrs.fr</p>	<p>BEDJAOUI-ALACHAHER Lamia Laboratoire de Recherche sur les Macromolécules Université de Tlemcen, BP19, 13000 Tlemcen Algeria l_bedjaoui@yahoo.fr</p>
<p>BERNAUDAT Florent Institut Laue-Langevin CS 20156, 38042 Grenoble Cedex 9, France bernaudatf@ill.fr</p>	<p>CAZARES CORTES Esther Laboratoire Matière Molle et Chimie - ESPCI Paris 10 rue Vauquelin, 75005 Paris, France esther.cazares-cortes@espci.fr</p>
<p>CARL Nico Oliver Institut Laue-Langevin CS 20156, 38042 Grenoble Cedex 9, France carlno@ill.fr</p>	<p>DANIEL Christophe Dipartimento di Chimica e Biologia Università degli studi de Salerno Via Giovanni Paolo II, 132-84084 Fisciano (SA), Italy cdaniel@unisa.it</p>
<p>DAS Sujoy Indian Association for the Cultivation of Science Jadavpur, 700032 Kolkata, India s.das648@gmail.com</p>	<p>DEL SORBO Giuseppe Rosario Institut Laue-Langevin CS 20156, 38042 Grenoble Cedex 9, France del-sorbo@ill.fr</p>
<p>DI RENZO Francesco Institut Charles Gerhardt Montpellier 240 Avenue Emile Jeanbrau, 34296 Montpellier direnzo@enscm.fr</p>	<p>FORSYTH Trevor Institut Laue-Langevin CS 20156, 38042 Grenoble Cedex 9, France tforsyth@ill.eu</p>
<p>FRAGNETO Giovanna Institut Laue-Langevin CS 20156, 38042 Grenoble Cedex 9, France fragneto@ill.fr</p>	<p>GRILLO Isabelle Institut Laue-Langevin CS 20156, 38042 Grenoble Cedex 9, France grillo@ill.fr</p>
<p>GUENET Jean-Michel Institut Charles Sadron Rue du Loess, 67034 Strasbourg jean-michel.guenet@ics-cnrs.unistra.fr</p>	<p>HADJ-HAMOU Assia Siham Laboratoire des Matériaux Polymères USTHB, BP 32 El-Alia, 16111 Bab-Ezzouar, Algeria hadjhamouassia@yahoo.fr</p>
<p>HARRIES Daniel Institute of Chemistry and The Fritz Haber Research Center, The Hebrew University, Jerusalem 91904, Israel daniel.harries@mail.huji.ac.il</p>	<p>HÄRTLEIN Michael Institut Laue-Langevin CS 20156, 38042 Grenoble Cedex 9, France haertlein@ill.fr</p>
<p>HERNÁNDEZ Rebeca Instituto de Ciencia y Tecnología de Polímeros Juan de la Cierva 3, 28006 Madrid rhernandez@ictp.csic.es</p>	<p>IM Hyeon-Gyun Korea Electrotechnology Research Institute KERI, 12 Bulmosan-ro 10 beon-gil, Changwon-si, Korea hgim@keri.re.kr</p>
<p>IKKALA Olli Molecular Materials, Department of Applied Physics, Aalto University, PO Box 15100, FIN- 00076 Aalto, Espoo, Finland olli.ikkala@aalto.fi</p>	<p>KANEKO Fumitoshi Osaka University, 1-1 Machikaneyama, 560-0043 Toyonaka, Japan toshi@chem.sci.osaka-u.ac.jp</p>
<p>KANG Dong Jun Korea Electrotechnology Research Institute 12 Bulmosan-ro 10 beon-gil, Changwon-si, Korea kangdj@keri.re.kr</p>	<p>KOŠOVAN Peter Department of Physical and Macromolecular Chemistry, Charles University, Hlavova, 12000 Prague, Czech Republic peter.kosovan@natur.cuni.cz</p>

<p>LE Cong Anh Khanh Centre de Recherches sur Les Macromolécules Végétales CS40700, 38041 Grenoble Cedex 9, France leconganhkhanh@gmail.com</p>	<p>LE MOIGNE Nicolas Centre des Matériaux des Mines d'Alès (C2MA), IMT Mines Alès, Université de Montpellier, 6 Av. de Clavières, 30319 Alès Cedex, France nicolas.le-moigne@mines-ales.fr</p>
<p>MAZARI Akkacha Laboratory of Storage and Valorization of Renewable Energies USTHB, BP 32 El-Alia, 16111 Bab-Ezzouar, Algeria chimi24@hotmail.fr</p>	<p>METREF Farid Laboratoire des Matériaux Polymères USTHB, BP 32 El-Alia, 16111 Bab-Ezzouar, Algeria fmetref2000@yahoo.fr</p>
<p>MITRAKI Anna Department of Materials Science and Technology, University of Crete and IESL/FORTH N. Plastira 100, Vassilika Vouton, Heraklion, Crete, Greece 71003 mitraki@materials.uoc.gr</p>	<p>MIZUTA Ryo University of Cambridge 9 JJ Thomson Avenue, CB3 0FA Cambridge, United Kingdom rm832@cam.ac.uk</p>
<p>MORFIN Isabelle Laboratoire Interdisciplinaire de Physique BP 87, 38402 Saint Martin d'Hères, France isabelle.morfin@univ-grenoble-alpes.fr</p>	<p>NANDI Arun K. Indian Association for the Cultivation of Science Jadavpur, 700032 Kolkata, India psuakn@iacs.res.in</p>
<p>NAVARRA Wanda Dipartimento di Chimica e Biologia Università degli studi di Salerno Via Giovanni Paolo II, 132-84084 Fisciano (SA), Italy wnavarra@unisa.it</p>	<p>NISHIYAMA Yoshiharu Centre de Recherches sur Les Macromolécules Végétales CS40700, 38041 Grenoble Cedex 9, France yoshiharu.nishiyama@cermav.cnrs.fr</p>
<p>OGAWA Yu Centre de Recherches sur Les Macromolécules Végétales CS40700, 38041 Grenoble cedex 9, France yu.ogawa@cermav.cnrs.fr</p>	<p>OUAAD Kamal Laboratoire des Matériaux Polymères USTHB, BP 32 El-Alia, 16111 Bab-Ezzouar, Algeria ouakamel@yahoo.fr</p>
<p>PLAZANET Marie Laboratoire Interdisciplinaire de Physique BP 87, 38402 Saint Martin d'Hères, France marie.plazanet@univ-grenoble-alpes.fr</p>	<p>PREVOST Sylvain Institut Laue-Langevin CS 20156, 38042 Grenoble Cedex 9, France prevost@ill.fr</p>
<p>PUTAUX Jean-Luc Centre de Recherches sur Les Macromolécules Végétales CS40700, 38041 Grenoble Cedex 9, France jean-luc.putaux@cermav.cnrs.fr</p>	<p>SCHWEINS Ralf Institut Laue-Langevin CS 20156, 38042 Grenoble Cedex 9, France schweins@ill.eu</p>
<p>STEPANEK Petr Institute of Macromolecular Chemistry AS CR Heyrovskeho nam. 2, 16206 Prague, Czech Republic stepanek@imc.cas.cz</p>	<p>WEIK Martin Institut de Biologie Structurale CS 10090, 38044 Grenoble Cedex 9, France weik@ibs.fr</p>