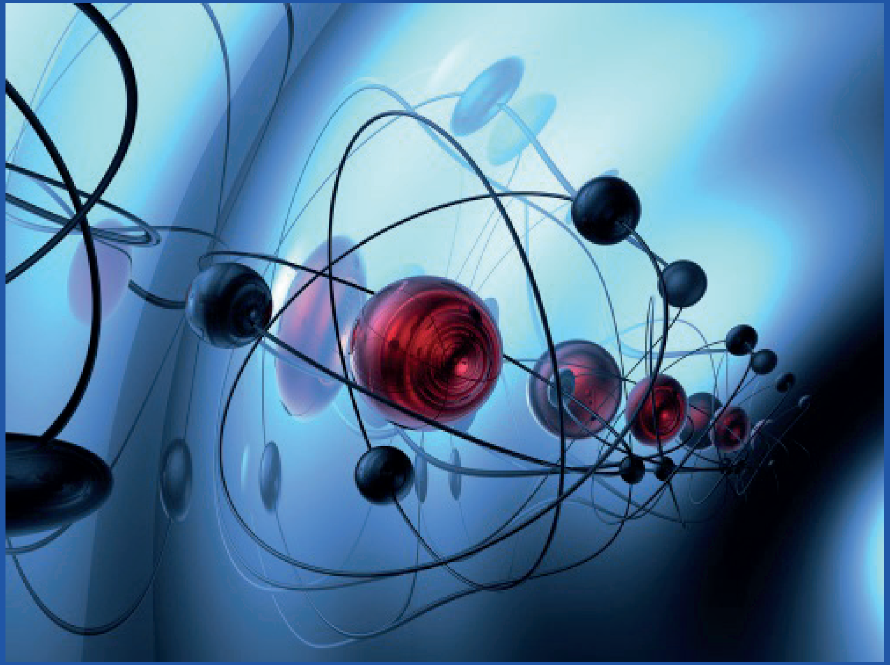
2nd Nordic-Italian Polymer Future workshop

2-3 September 2019



Abstracts of invited lectures

Oral presentations

2nd Nordic-Italian Polymer Future workshop

2-3 September 2019, IDA Congress Center, Copenhagen

Abstracts of invited lectures

Polymer Nanostructures for Photonics: Novel opportunities from Lasing to Sensing

Davide Comoretto
Department of Chemistry
and Industrial Chemistry
Università di Genova, Italy

davide.comoretto@unige.it

The field of photonics is traditionally dominated by inorganic materials both as semiconductors or insulators. Such materials are often patterned in nanostructures suitable to manage light propagation and emission or fostering light in/out-coupling with bulk devices. To mold the flux of the light, photonic crystals (PhC), i.e. highly ordered structures where different refractive index systems are arranged into periodic submicrometric lattices, are of paramount importance. [1]

Recently, polymer and colloidal materials processable from solutions and/or from melt stimulated the development of PhCs with unprecedented properties for their inorganic counterpart like mechanical flexibility, gas permeability and stimuli responsivity. Moreover, such polymer PhC allows to embed into their structure advanced photoactive materials such as conjugated polymers, quantum dots, hybrid perovskites, self-assembling supramolecular systems, which can pave the way toward novel technologies. [2, 3]

Among polymer PhCs, distributed Bragg reflectors (DBRs), i.e. alternated multilayers of different polymers stacked one in top to the other, represent a simple playground to develop novel macromolecular materials and to tackle technological challenges. Indeed, they have been demonstrated very efficient and performant to prepare large area flexible laser cavities, to control light emission, to improve the efficiency of photovoltaic devices, and to make label-free colorimetric sensors.3
In this lecture, we will provide an overview of the opportunities provided by polymer PhC discussing factors limiting their performances and applications, hopefully stimulating collaborations between research groups involved in Nordic-Italian Meeting.

---

1 J. D. Joannopoulos, S. G. Johnson, J. N. Winn, R. D. Meade, Photonic Crystals: Molding the Flow of Light, Princeton University Press, Woodstock 2011
2 D. Comoretto, Organic and Hybrid Photonic Crystals, Springer, Cham, Switzerland 2015.
3 P. Lova, G. Manfredi, and D. Comoretto, Adv. Optical Mater. 2018, 6, 1800730.

Towards Commercialization of Polymer Brushes

Mikkel Kongsfelt
RadiSurf ApS, Arresoevej 5B
DK-8240 Riskov, Denmark

mikkel@radisurf.com

The technology of polymer brushes on hard surfaces, has been hailed as one of the top achievements within nanoscience and polymer chemistry in the last 30 years. [1] More than 40.000 scientific papers has been published on the subject. With chemical bonds to the substrate surface, a unique dense structure, and the ability to tune the chemistry of these polymers, they hold promise for a broad amount of applications. Controlling the chemistry and physical structure has been used to show applications like friction control, anti-fouling properties, adhesion properties and surface protection.

However, the dense polymer brush structures are only obtainable by chemically growing the polymers from the surface – a chemically difficult process to control and scale. Surface Initiated Atom Transfer Radical Polymerization (Si-ATRP) has been the best applicable method for many years, despite that this process is a difficult process and hard to control outside a laboratory environment. This has been the largest barrier to any commercialization of polymer brush-based technologies. However, in recent years new developments have created variations of the controlled radical polymerizations like ICAR ATRP, ARGET ATRP, SARA ATRP, eATRP, and photoinduced ATRP and most recently single-electron transfer living radical polymerization (SET-LRP). All these developments have opened new hope and opportunities for scaling up surface initiated controlled radical polymerizations.

We have combined the knowledge from many years of research into a process that allows scaling up the technology under industrially relevant conditions.

---

[1] Macromolecules 2017, 50, 11, 4089-4113

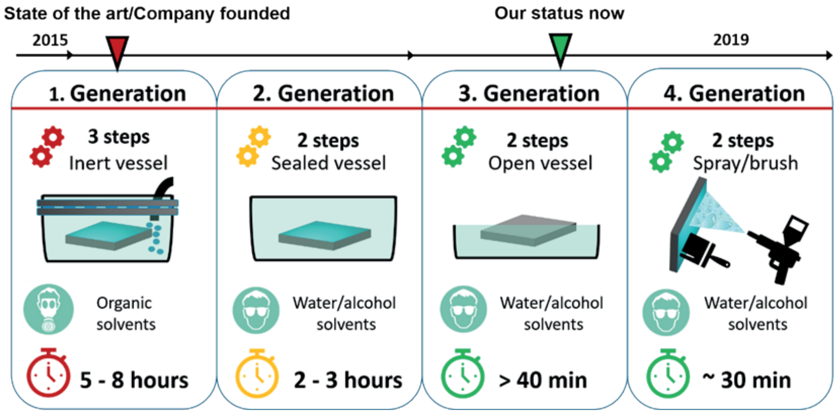


Figure 1: Our development of the polymer brush formation technologies since founding RadiSurf. From 1. Generation (ATRP based), to an industrially relevant process (3rd and 4th generation).

Kinetic Pathways for Block Copolymer Self-assembly in Solution

Reidar Lund
Department of Chemistry,
University of Oslo
Blindern 0315 Oslo, Norway.

reidar.lund@kjemi.uio.no

Self-assembled systems are generally highly dynamic structures characterized by molecular exchange, fluctuations and fusion/fission and morphological transitions. Examples include micelles formed by synthetic surfactants and block copolymers as well as lipid membranes. Despite their importance in technological and biomedical applications, the kinetic pathways associated with the formation and molecular transport of such self-assembled nanostructures are generally poorly understood. Time-resolved small-angle X-ray/neutron scattering (TR-SAXS/SANS) is powerful technique [1] that allow non-equilibrium kinetic processes such as nucleation processes [2,4] and morphological transitions [3,5] to be followed with structural resolution over time scales starting from a few milliseconds. Neutrons have the additional advantage of facile contrast variation through H/D substitution schemes, which also allow equilibrium processes such as molecular exchange and diffusion to be studied without perturbation [1,6-8].

In this presentation we will address the basic kinetic pathways found in block copolymer micelles formed by amphiphilic self-assembly and complexation (“coacervation”). We will address both equilibrium and non-equilibrium kinetics and argue that the understanding of kinetic pathways can be utilized to manipulate and design the physical properties of self-assembled systems. Furthermore, we shall discuss the role of confinement and crystallinity on the stability and molecular transport processes in semi-crystalline micelles [8,10] and discuss the relevance to biological systems and biomedical applications.

---

1 R. Lund, L. Willner and D. Richter, Adv Polym Sci, 2013, **259**, 51–158.
2 R. Lund, L. Willner, M. Monkenbusch, P. Panine, T. Narayanan, J. Colmenero and D. Richter, Phys. Rev. Lett., 2009, **102**, 188301.
3 R. Lund, L. Willner, D. Richter, P. Lindner and T. Narayanan, ACS Macro Lett., 2013, **2**, 1082–1087.
4 G. V. Jensen, R. Lund, J. Gummel, M. Monkenbusch, T. Narayanan and J. S. Pedersen, J. Am. Chem. Soc., 2013, **135**, 7214–7222.
5 G. V. Jensen, R. Lund, J. Gummel, T. Narayanan and J. S. Pedersen, Angew. Chem. Int. Ed., 2014, **53**, 11524–11528.
6 R. Lund, L. Willner, J. Stellbrink, P. Lindner and D. Richter, Phys. Rev. Lett., 2006, **96**, 068302.
7 S.-H. Choi, T. P. Lodge and F. S. Bates, Phys. Rev. Lett., 2010, **104**, 047802.
8 T. Zinn, L. Willner and R. Lund, Phys. Rev. Lett., 2014, **113**, 238305.
9 T. Zinn, L. Willner, V. Pipich, D. Richter and R. Lund, ACS Macro Lett., 2015, **4**, 651–655.
10 König, N., Willner, L., Pipich, V., Zinn, T., & Lund, R. Phys. Rev. Lett, 2019. 122(7), 078001.

Amphiphilic Polymers by Means of Light Scattering Methods

Lecture presents several modern topics developing at the Department of Chemistry by means of light scattering methods. Amphiphilic and thermally responsive polymers in aqueous solutions are discussed. Mass, size, shape of such macromolecules, their self-assembling behavior as well as chains dynamics are presented as functions of changing temperature or/and the solvent composition.

Vladimir Aseyev
Department of Chemistry
University of Helsinki
FIN-00014 HY Helsinki, Finland

vladimir.aseyev@helsinki.fi

Chitosan (Nano)composites as Adsorbents for Water Purification: Challenges and Opportunities

Martina Salzano de Luna
Department of Chemical,
Materials and Industrial
Production Engineering
University of Naples Federico II, Italy

martina.salzanodeluna@unina.it

Because of the rapid development of the economy and the modern industry, environmental issues are becoming a major focus of scientific attention. Water contamination is among the most critical concerns of our era. In particular, water pollution due to the disposal of large amounts of dye-bearing wastewater from tannery, textile, paper, and plastic industries is a serious issue. To tackle this problem, adsorption of contaminants onto suitable substrates has been recognized as a feasible and versatile approach. A great scientific and technological interest thus exists in identifying new and effective adsorbent materials. In this regard, chitosan (CS) is often regarded as one of staple materials for the development of environmentally friendly adsorbents for water purification purposes. Over the last decade, a number of CS-based materials have been developed and studied, and some of them also exhibited outstanding performances. Although CS is highly effective for the removal of specific classes of contaminants, its adsorption capacity is not broad-spectrum. Only few examples of highly performing broad-spectrum CS-based adsorbents have been successfully proposed, and actually the literature in this field is growing but is still rather poor.

Here, the use of chitosan for the development of highly performing (nano)composites adsorbents will be critically discussed, highlighting the main strengths and drawbacks of this natural polymer. In addition, different strategies for the design and realization of chitosan-based (nano)composite adsorbents that exhibit a good affinity towards a different array of contaminants will be reviewed and discussed.

Fungal Biopolymers: A New Source for Production of Bioplastics

Akram Zamani
Department of Resource Recovery
and Building Technology
University of Borås, Sweden

akram.zamani@hb.se

The need to replace conventional synthetic plastics has led to development of a rich and diverse field of research in bioplastic production. Fungal biopolymers are a promising, but hitherto largely unexplored source for bioplastics production. Fungal biomass is a rich source of different biopolymers such as proteins, chitin, chitosan, and glucans. Production of fungi does not require agricultural lands and therefore fungal biomass is reproducible with a low environmental footprint. Fungi can grow quickly on low cost substrates e.g., food and agricultural wastes. Bioplastics in different basic forms e.g., thin films, 3D objects, and yarns can be produced from fungal biopolymers for different applications.

Properties of Polyelectrolyte Multilayers - Beyond Electrostatic Stabilization

Esben Thormann
Department of Chemistry
Technical University of Denmark

esth@kemi.dtu.dk

Polyelectrolyte multilayers are typical two-component polyelectrolyte films assembled by a layer-by-layer process. In most cases, the buildup of a multilayered film is based on alternate adsorption of oppositely charged polymers through electrostatic attraction. As electrostatic attraction is the main driving force for the multilayer buildup, it also means that the layer structure will be markedly influenced by for example the ionic strength. For multilayers of weak polyelectrolytes, e.g. layers of alginate and chitosan, the layer composition will further be strongly dependent of the pH during layer buildup. The fact that the charge density of weak polyelectrolytes varies with pH however also limits the stability of such layers. For instance, changes in pH can disrupt the charge neutrality condition within the film and give rise to uncontrolled swelling, which results in instantaneous disintegration of the film. By introduction of aldehyde groups on the alginate chains, we have demonstrated a chemical stabilization of the layers due to formation of Schiff bases. While much work on multilayers concerns biopolymers, the use of synthetic polymers provides a wide range of new opportunities. Uncharged polymers with desired functionalities can inspire the design of random copolymer containing a controlled number of charged monomer enabling multilayer assembly. In another work we have demonstrated how this approach can be used to form single component polyPEGMEMA multilayer films and how such films can be post-functionalized in order to selectively quench the charges in the layer of to modify the surface properties of the layer.

Polymer Films with Aggregation-induced Emission: Applications and Perspectives

Andrea Pucci
Department of Chemistry
and Industrial Chemistry
Università di Pisa, Italy

andrea.pucci@unipi.it

In this contribution, the use of fluorophores with Aggregation-Induced Emission (AIE)1 features is discussed for application in materials science as probes for sensing and energy harvesting. Notably, AIE systems with donor–acceptor structure are also called Fluorescent Molecular Rotors (FMRs). In FMRs, the AIE effect is often ascribed to a non-emissive twisted intramolecular charge transfer (TICT) state which occurs in solution, whereas in aggregates or in viscous media, transition from locally excited to TICT is inhibited. Those molecules have become rather popular in the last 5–10 years thanks to their easy applicability as non-mechanical viscosity sensors, tools for protein characterization, and local microviscosity imaging.2-4 In polymers, AIE and FMR fluorophores are promising candidates to overcome all the fluorescence deactivation pathways due to fluorophore aggregation. Their intense fluorescence emission helps in both sensing and energy harvesting applications, thus enabling the development of high performance plastic devices. Fluorescence also plays a pivotal role in solar energy harvesting in luminescent solar concentrators (LSCs).5-7 In LSCs, sunlight penetrates the top surface of an inexpensive plastic or glass waveguide. This light is absorbed by luminescent molecules which are either embedded in the waveguide or applied in a separate layer on top or bottom of the waveguide. A fraction of the re-emitted light is trapped in the waveguide by total internal reflection and then collected at the edges of the device to produce electric power by means of photovoltaic cells even with a cloudy sky.

We expect that these concepts assisted by sustainable routes may steer innovative, smart and intelligent materials to be used in the everyday life.

---

1 J. Mei, N. L. C. Leung, R. T. K. Kwok, J. W. Y. Lam and B. Z. Tang, Chemical Reviews, 2015, **115**, 11718-11940.

2 N. Guidugli, R. Mori, F. Bellina, B. Z. Tang and A. Pucci, in Principles and Applications of Aggregation-Induced Emission, eds. Y. Tang and B. Z. Tang, Springer International Publishing, Cham, Editon edn., 2019, pp. 335-349.

3 C. Sorgi, E. Martinelli, G. Galli and A. Pucci, Science China Chemistry, 2018, **61**, 947-956.

4 P. Minei, M. Koenig, A. Battisti, M. Ahmad, V. Barone, T. Torres, D. M. Guldi, G. Brancato, G. Bottari and A. Pucci, Journal of Materials Chemistry C, 2014, **2**, 9224-9232.

5 B. McKenna and C. Evans Rachel, Advanced Materials, 2017, **29**, 1606491.

6 A. Pucci, Israel Journal of Chemistry, 2018, **58**, 837-844.

7 R. Mori, G. Iasilli, M. Lessi, A. B. Muñoz-García, M. Pavone, F. Bellina and A. Pucci, Polymer Chemistry, 2018, **9**, 1168-1177.

Counterion Responsive Polycations

Erno Karjalainen
Department of Chemistry
University of Helsinki, Finland

erno.karjalainen@helsinki.fi

The effect of the small molecular counterions on the properties of polycations in significant. Most notably, the solubility of cationic polymers and their glass transition temperatures can be considerably influenced by the choice of the anion. In this way, very non classical polyelectrolytes that are insoluble in water and have glass transition temperatures below room temperature can be synthesized. [1-3] The high anion sensitivity of the material also opens up the possibility of post polymerization tuning of material properties by simple and effective ion exchange reactions. This opens novel avenues for straightforward synthesis of many different materials from a parent polymer utilizing ionic interactions.

The focus of this talk will be on aqueous solution properties of cationic polymers and their response to non-classical counterions. The ionic interactions allow the tuning of thermal response of the polymers that have a lower critical solution temperature (LCST) type transition in water. [4, 5] It is also possible to induce thermoresponsive behavior to polyelectrolytes that are completely soluble in water by introduction of mixtures of anions into solutions in situ. [6] Also the topic of modifying properties of crosslinked polymer films by ion exchange will be discussed. [7]

---

1. Marcilla, R.; Blazquez, J. A.; Rodriguez, J.; Pomposo, J. A.; Mecerreyes, D. J. Polym. Sci. Part A 2003, 42, 208-212.
2. Marcilla, R.; Blazquez, J. A.; Fernandez, R.; Grande, H.; Pomposo, J. A.; Mecerreyes, D. Macromol. Chem. Phys. 2005, 206, 299-304.
3. Green, M. D.; Salas-de la Cruz, D.; Ye, Y.; Layman, J. M.; Elabd, Y. A.; Winey, K. I.; Long, T. E. Macromol. Chem. Phys. 2011, 212, 2522-2528.
4. Karjalainen, E.; Aseyev, V.; Tenhu, H. Macromolecules 2014, 47, 2103-2111.
5. Karjalainen, E.; Aseyev, V.; Tenhu, H. Polym. Chem. 2015, 6, 3074-3082.
6. Karjalainen, E.; Aseyev, V.; Tenhu, H. Macromolecules 2014, 47, 7581-7587.
7. Karjalainen, E.; Wales, D. J.; Gunasekera, D. H. A. T.; Dupont, J.; Licence, P.; Wildman, R. D.; Sans, V. ACS Sustainable Chem. Eng. 2018, 6, 3984-3991.

Sustainable and Functional Polymer Design through Ring-opening Polymerization

Karin Odelius
Department of Polymer
and Fibre Technology,
KTH Royal Institute of Technology
SE-100 44 Stockholm, Sweden

hoem@kth.se

To achieve sustainable polymeric materials, several different puzzle pieces need to be considered. These range from the building-block sources and the synthesis pathways all the way to the product's end-of-use treatment. Each of these pieces have numerous challenges that need to be tackled, yet optimization of the overall system is the key goal. Ring-opening reactions fulfil several features contributing to sustainable polymeric materials, including the possibility of using renewable building-blocks and, with the proper choice of reaction system, synthetic routes. This presentation will outline ring-opening polymerization (ROP) of two very promising material groups: the aliphatic polyesters and polycarbonates. ROP contributes with some very important aspects such as the possibility of both high activity (fast reaction rates) and high selectivity (control over molecular weight, low Đ, end-group control) and the possibility to incorporated functionality for further reactions. As ROP is a thermodynamic equilibrium reaction and the ceiling temperatures of some of the monomers are comparably low, the reaction conditions can also be utilized to push the reaction either towards the monomer or the polymer. It is thereby possible to achieve well defined sustainable functional polymers that after use can be recycled back to cyclic monomer simply by altering the surrounding environment. Hence, ROP of well-defined aliphatic polyesters and polycarbonates will be detailed as sustainable polymeric materials.

Self-assembling Materials for Nanoscale Metrology

Federico Ferrarese Lupi
Advanced Materials and Life Sciences
Istituto Nazionale Di Ricerca
Metrologica (INRiM)
10135 Torino, Italy

f.ferrareselupi@inrim.it

The continuous technological progress pervading the various scientific fields composing nanotechnology leads to the demand for an increasingly high degree of control in the fabrication of nanometric devices and systems. The milestone of this progress is the capability to control, with high accuracy and precision, both the dimensional positioning and the chemical composition of small features, with typical size at sub-20 nm level. The achievement of this capability is a mandatory step in the development of applied science such as microelectronics, photonics and nano-metrology. In order to sustain such processes the implementation of reliable characterization techniques and metrology standards is needed, along with the introduction of new types of reference samples at the nanoscale, such as nanometric length standards or calibration samples for 3D analytical techniques.
In this lecture we will show how the use of self-assembling polymeric materials, such as block copolymers or colloidal nanospheres, can guide the development of nano-metrology standards beyond the state of the art.

2nd Nordic-Italian Polymer Future workshop

2-3 September 2019, IDA Congress Center, Copenhagen

Oral presentations

Tie chains and trapped entanglements - ghosts in traditional experiments but apparent in simulations and for fracture toughness

U. W. Gedde[a], M. S. Hedenqvist[a], F. Nilssona,
T. Gkourmpis[b] and A. Moyassari[a]

a Fibre and Polymer Technology,
School of Engineering Sciences of Chemistry,
Biotechnology and Health,
KTH Royal Institute of Technology,
SE-100 44 Stockholm, Sweden.

b Innovation & Technology,
Borealis AB, SE-444 86 Stenungsund,
Sweden.

The concentrations of tie chains and trapped entanglement in semicrystalline polymers is believed to be the factor that controls the fracture toughness of the polymer. There is, however, no experimental technique that can provide a direct assessment of the concentrations of these species. The only feasible way to obtain more accurate quantitative information about the concentration of tie chains and trapped entanglements is by modelling or simulation. One method is to use Monte Carlo methods to build the crystal-amorphous interphase. A Monte Carlo method was developed by Nilsson et al. (2012) using a stack of crystal and amorphous layers. The dimensions of the layered structure were given by experimental data for the long period and crystallinity. Molecules were placed in the stack and certain rules were applied to establish their conformations: (i) chain ends were confined to the amorphous regions; (ii) the concentration of tight folds was controlled by keeping the amorphous density at 85 % of the crystal density, i.e. the molar fraction of tight folds was an adjustable parameter; (iii) the molecular entries to the amorphous phase were according to an actual crystal unit cell; (iv) the statistical amorphous chains were built by the phantom chain statistics at the actual temperature and the tour terminated when the amorphous chain touched a crystal surface, either in the crystal which it originally left (forming a loop) or in a neighbouring crystal forming a tie chain or a statistical loop; (v) an optimum degree of filling of the system volume turned out to be 50 %; (vi) an algorithm for identifying trapped entanglements was developed based on knot theory. The concentrations of both tie chains and trapped entanglements show a marked increase with increasing molar mass reaching a plateau at approximately 1000 kg mol–1. The concentration of trapped entanglements is approximately 2.5 times greater than that of the tie chains. These data suggest that both tie chains and trapped entanglements need to be assessed in order to provide a structural basis for fracture toughness. A series of branched polyethylenes was simulated using the same method as that used for linear polyethylenes (Moyassari et al. (2015)). It was assumed that branches were rejected from the crystal regions, and this led to overcrowding in the amorphous regions. The tight folding could not be given the right statistical weight, because in many such attempts a tight fold required the housing of branches in the crystal phase which was not allowed and this gave the statistical chains too high a statistical probability, which resulted in overcrowding of the amorphous phase. The origin of this problem was essentially the statistical placement of the branches; each polymer molecule was in fact a multicomponent with regard to crystallization. The solution to the problem is to build a stack with different crystal thicknesses, to sort the stems according to length, to reassemble the pieces into polymer chains and to allow them to crystallize in a suitably thick crystal. This was the segregation performed by the simulation algorithm which, together with another change of the algorithm allow-

---

Nilsson, F., Lan, X., Gkourmpis, T., Hedenqvist, M. S. and Gedde, U. W. (2012) *Polymer*, **53**, 3594. Moyassari, A., Mostafavi, H., Gkourmpis, T., Hedenqvist, M. S., Gedde, U. W. and Nilsson, F. (2015) *Polymer*, **72**, 177. Moyassari, A. Unge, M., Hedenqvist, M. S., Gedde, U. W. and Nilsson, F. (2017) *J. Chem. Phys.*, **146**, 20204901. Moyassari, A., Gkourmpis, T., Hedenqvist, M. S. and Gedde, U. W. (2019a) *Polymer*, **161**, 139. Moyassari, A., Gkourmpis, T., Hedenqvist, M. S. and Gedde, U. W. (2019b) *Macromolecules*, **52**, 807.

Structure property relationships of ultra-high drug loaded polymer micelles. Effects of the hydrophobic core and the hydrophilic corona.

M. M. Lübtow[1], M. S. Haider[1], L. Hahn[1],
R. Luxenhofer[1]

- Functional Polymer Materials, Chair for
Advanced Materials Synthesis, Department

Chemistry and Pharmacy,
Julius-Maximilians-University Würzburg,
Röntgenring 11,
97070 Würzburg,
Germany

A large fraction of active pharmaceutical ingredients (API) suffer from poor water-solubility and concomitant poor bioavailability. Polymeric excipients can be used to increase the apparent water solubility of insoluble compounds, suppress drug crystallization and thus, increase their bioavailability. However, the amount of API that can be stably dispersed in an amorphous manner is often rather limited.

We have previously reported on a novel polymer platform, which is allows to formulate unusually large amounts of the extremely water insoluble paclitaxel [1,2,3] and other APIs and API combinations [4] with up to 50 wt.% incorporated in the polymer micelles. More recently, we have found very pronounced effects of very small structural variations on the formulation capacity for curcumin, another highly insoluble natural compounds [5-9]. In this presentation, the most recent finding regarding the structure-property relationships which enable such unusual high drug loading will be discussed as we get closer to the goal to gain comprehensive understanding of the molecular interactions within this novel excipient platform for extremely water insoluble APIs.

---

1 R. Luxenhofer, A. Schulz, C. Roques, S. Li, T. K. Bronich, E. V. Batrakova, R. Jordan, A. V. Kabanov, Biomaterials **2010**, 31, 4972.
2 A. Schulz, S. Jaksch, R. Schubel, E. Wegener, Z. Di, Y. Han, A. Meister, J. Kressler, A. V. Kabanov, R. Luxenhofer, C. M. Papadakis, R. Jordan, ACS Nano **2014**, 8, 2686.
3 Z. He, X. Wan, A. Schulz, H. Bludau, M. A. Dobrovolskaia, S. T. Stern, S. A. Montgomery, H. Yuan, Z. Li, D. Alakhova, M. Sokolsky, D. B. Darr, C. M. Perou, R. Jordan, R. Luxenhofer, A. V. Kabanov, Biomaterials **2016**, 101, 296.
4 Y. Han, Z. He, A. Schulz, T. K. Bronich, R. Jordan, R. Luxenhofer, A. V. Kabanov, Mol. Pharm. **2012**, 9, 2302.
5 M. M. Lübtow, L. Hahn, M. S. Haider, R. Luxenhofer, J. Am. Chem. Soc **2017**, 139, 10980.
6 L. Hahn, M. M. Lübtow, T. Lorson, F. Schmitt, A. Appelt-Menzel, R. Schobert, R. Luxenhofer, Biomacromolecules **2018**, 19, 3119.
7 M. M. Lübtow, L. C. Nelke, J. Seifert, J. Kühnemundt, G. Sahay, G. Dandekar, S. Nietzer, R. Luxenhofer, J. Control. Release **2019**, 303, 162.
8 M. M. Lübtow, M. S. Haider, M. Kirsch, S. Klisch, R. Luxenhofer, Biomacromolecules **2019**, in print, DOI: 10.1021/acs.biomac.9b00618.
9 M. M. Lübtow, H. Marciniak, A. Schmiedel, M. Roos, C. Lambert, R. Luxenhofer, ChemEurJ **2019**, in print, DOI: 10.1002/chem.201902619.

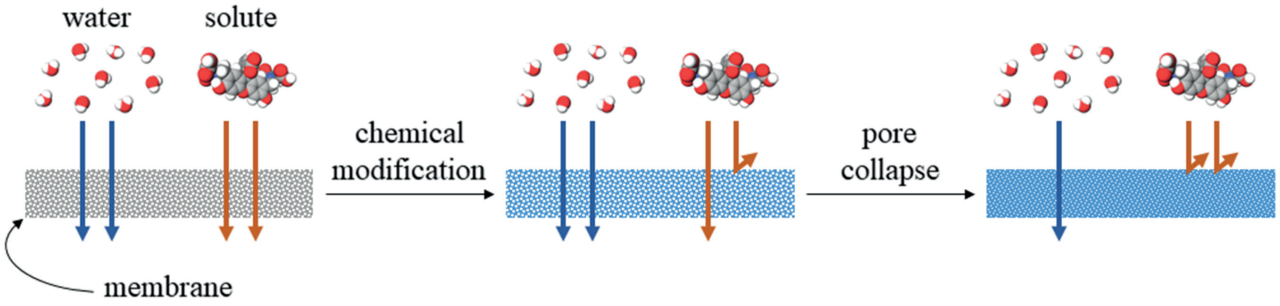
From ultrafiltration to nanofiltration by controlled pore collapse of modified polyethersulfone membranes

Libor Zverina, Manuel Pinelo,
John M. Woodley, **Anders E. Daugaard***
Danish Polymer Centre,
Department of Chemical and
Biochemical Engineering,
Technical University of Denmark,
Building 227,
2800 Kgs. Lyngby,
Denmark

* adt@kt.dtu.dk

Polyethersulfone is a widely used ultrafiltration membrane material thank to its good film-forming and membrane-forming properties, thermal stability, chemical inertness, and mechanical strength. Polyethersulfone membranes find a range of applications in food processing, biomedical field, and water-treatment technologies. To further extend the application range of these membranes, there is a strong need for control over membrane properties.

Here we demonstrate how modification of membrane surface chemistry can be used to control the extent of pore collapse and ultimately to tailor membrane properties. Commercial hollow-fiber polyethersulfone membranes were activated by a heterogeneous reaction introducing benzyl chloride functionality to the surface, from which surface-initiated atom transfer radical polymerization (SI-ATRP) of several monomers was conducted [1]. The polymer grafts could be used for controlling the water flux and solute retention characteristics of the membranes (Figure 1). The modified membranes were subsequently dried to facilitate pore collapse or protected from collapse by use of glycerol. The chemical nature of the grafted polymer was directly reflected in the water flux-to-retention ratio of the treated membranes and the extent of pore collapse. Finally, it will be shown how the controlled membrane pore collapse could be exploited to obtain membranes showing even higher solute retention.



---

[1] Hoffmann, C.; Silau, H.; Pinelo, M.; Woodley, J. M.; Daugaard, A. E. Surface modification of polysulfone membranes applied for a membrane reactor with immobilized alcohol dehydrogenase. Mater. Today Commun. 2018, 14, 160–168

Visible Light Responsive Polymer Nanocapsules

Valentina Marturano[1], Veronica Ambrogi[1],
B. Tylkowski[2], M. Giamberini[3],
Pierfrancesco Cerruti[4]

1 Department of Chemical, Materials
and Production Engineering (DICMAPI),
University of Naples “Federico II”,
P.le Tecchio, 80, 80125 Napoli, Italy

2 Chemistry Technology Centre of Catalonia
(CTQC), C/Marcel-lí Domingo,
43007 Tarragona, Spain

3 Department of Chemical Engineering (DEQ),
Universitat Rovira i Virgili, Av. Països Catalans,
26, 43007 Tarragona, Spain

4 Institute for Polymers, Composites
and Biomaterials, National Council of Research,
Via Campi Flegrei, 34, 80078 Pozzuoli, Italy

valentina.marturano@unina.it

Photo-responsive polymer nanocapsules [1] have been the center of extensive experimental and industrial efforts for their positive performance as drug delivery systems as well as their promising applications in crop protection, food packaging, and household products.

In this work, we report on the preparation of visible light responsive nanocapsules loaded with thyme essential oil and a fluorescent probe molecule, Coumarin-6. The photosensitive polyamide shell, containing visible light-sensitive ortho-substituted azobenzene moieties in the main chain, was prepared by oil-in-water interfacial polycondensation in miniemulsion [2].

The light-responsive behavior of the modified azobenzene moieties, synthesized according to a modified procedure reported in literature [3], was assessed via UV-vis spectrometry before and after irradiation with visible light at different wavelengths. Nanocapsules dimension and morphology was evaluated via Dynamic Light Scattering (DLS) and Electron Microscopy (SEM ad TEM). Light-induced modifications in the capsules size and morphology were analyzed using Atomic Force Microscopy (AFM) and the triggered release of the encapsulated essential oil and Coumarin-6 were monitored by means of UV-vis spectroscopy and spectrofluorimetry respectively.

Overall, this work provides an interesting insight on the preparation and characterization of visible light responsive polymer nanocapsules. Visible light is readily available and un-harmful to human beings. For this reason, the described polymeric nanoplatforms could be interesting for a wide range of commodity and specialty applications.

---

1 V. Marturano, P. Cerruti, M. Giamberini, B. Tylkowski, V. Ambrogi. Polymers, 9, 1-8, (**2016**).
2 V. Marturano, V. Bizzarro, A. De Luise, A. Calarco, V. Ambrogi, M. Giamberini, B. Tylkowski, P. Cerruti, Nano Research, 11(5), 2783-2795 (**2018**).
3 B. Tylkowski, M. Giamberini, T. Underiner, S.F. Prieto, J. Smets, Macromolecular Symposia, 360, 192-197 (**2016**).

A Simple Optical Method for the Assessment of Molecular Diffusion Coefficients and Sensing Using Polymer Thin Films

Paola Lova*, Davide Comoretto

Dipartimento di Chimica e Chimica Industriale,
Università degli Studi di Genova,
Genova, Italy

*Email: paola.lova@edu.unige.it

In this work we show that the optical response of polymer multilayers called distributed Bragg reflectors (DBRs) can be easily employed to detect and identify molecular species and to assess their diffusion coefficients in the polymer themselves. DBRs are planar structures made of transparent films alternated periodically with submicrometric thickness and with different refractive index.[1] The interaction between these structures and light provides diffraction patterns which can be seen by the naked eye as bright iridescent colors. When small molecules intercalate within them, their dynamic optical response allows to recognise the chemical specie and to assess its diffusion coefficient in the polymer themselves.[2]

As a proof of principle, we propose DBRs made of commodity polymers (polystyrene and cellulose acetate) to assess short chain alcohols. We choose analytes with similar polarity, weak-bonding with the polymer matrices, and molecular size that represent a challenge in term of discrimination. Notwithstanding such similarities, the response of the DBRs shows characteristic dynamics that allows to retrieve optical sorption-curves delivering different information for any analyte.[3, 4] This process allows to discriminate them and calculate diffusion coefficients in agreement with gravimetric data.

The method can also be demonstrated for several other chemical species including non-polar volatile organic compounds and fluorinated molecules.[1, 3, 5, 6] Then, these structure provide a substrate for qualitative and quantitative assessment of air quality through a simple easy-to-use colorimetric measurement. We explain the capability to discriminate the analytes intercalating in the structure in term of Hansen and Flory-Hugging parameters and believe that these sensors could tackle the lack of methods for the real-time quali-quantitative air monitoring in urban and industrial environments, which currently requires long-time sampling, separation processes and laboratory analyses.[7] We also believe that, thanks to the ease of mass-scale fabrication of polymer DBRs and their ease of integration with packaging technologies,[8] this method will be industrially relevant for the in-situ assessment of diffusive processes of degradation by-products, humidity or even oxygen in smart packaging systems for foods and optoelectronic devices.

---

[1] Lova, P.; Manfredi, G.; Comoretto, D. Adv. Opt. Mater. https://doi.org/10.1002/adom.201800730, (2018)

[2] Lova, P.; Manfredi, G.; Bastianini, C.; Mennucci, C.; Buatier de Mongeot, F.; Servida, A.; Comoretto, D. Submitted. (2018)

[3] Lova, P.; Manfredi, G.; Boarino, L.; Comite, A.; Laus, M.; Patrini, M.; Marabelli, F.; Soci, C.; Comoretto, D. ACS Photonics. 2, 537-543, (2015)

[4] Lova, P.; Bastianini, C.; Giusto, P.; Patrini, M.; Rizzo, P.; Guerra, G.; Iodice, M.; Soci, C.; Comoretto, D. ACS Appl. Mater. Interfaces. 8, 31941–31950, (2016)

[5] Giusto, P.; Lova, P.; Manfredi, G.; Gazzo, S.; Srinivasan, B.; Radice, S. V.; Comoretto, D. ACS Omega. 3, 7517-7522, (2018)

[6] Lova, P. Polymers. 10, 1161, (2018)

[7] Koppmann, R., Volatile Organic Compounds in the Atmosphere. John Wiley & Sons: Cambridge, UK, 2008.

[8] Song, H.; Singer, K.; Lott, J.; Wu, Y.; Zhou, J.; Andrews, J.; Baer, E.; Hiltner, A.; Weder, C. J. Mater. Chem. 19, 7520-7524, (2009)

Isosorbide and lignin as aromatic building blocks candidates for tailoring bio based thermosets with tunable property

Yunsheng Xu, Karin Odelius,
Minna Hakkarainen
Department of Fibre
and Polymer Technology,
KTH Royal Institute
of Technology,
Stockholm Sweden

E-mail: yunsheng@kth.se

Aromatic building blocks (e.g. bisphenol A, isophthalic acid) are commonly utilized to develop commercial thermosets as they can endow the thermoset with high thermomechanical properties. To develop biobased thermoset with comparable properties to replace the current petroleum analogs, the key point is to find suitable biobased aromatic building block candidates and to develop facile synthesis routes to fabricate the thermosets.

In our work, we have utilized renewable monomers directly (e.g. isosorbide and lignin) to synthesize biobased thermoset candidates with wide property window for replacement of commercial petroleum based thermosets. Attracted by the bicyclic ring structure of isosorbide, we have developed a series of biobased unsaturated polyesters (UPs) and a reactive diluent (RD) based on the isosorbide as core component in the resins.1 The fabricated thermosets had superior thermal and mechanical properties compared to most biobased UP thermosets with glass transition temperatures around 57–84 °C and a flexural modulus at 25 °C varying between 0.5 and 3.0 GPa, which is comparable to commercial unsaturated polyester thermosets. Another series of promising polyester thermosets were designed based on lignin, which is a macromolecule with aromatic backbone structure. By changing the feed ratio of lignin from 20 to 40%, the mechanical properties of the lignin thermosets could be tuned, with young's modulus ranging from 2.5 MPa to 1.3 GPa. A selected lignin thermoset also exhibited a superb shape memory property with shape fixity ratio of 95 % and shape recovery ratio of 99%. 2 The methods above and the synthesized biobased thermosets give promise for utilizing isosorbide and lignin to develop high-performance biobased thermosets for variety of applications.

Furthermore, considering lignin's heterogeneous structure and poor solubility in common solvents, which restrict its' use as a thermoset precursor, we also developed a process producing high yield of well-defined lignin oligomers. The process took place in a microwave under mild noncatalytic conditions and utilized in green solvents, and moderate temperatures (80-160°C). The easy preparation, narrow dispersity and rich aromatic structure, makes these oligomers interesting precursors for future thermoset synthesis.

---

1 Y. Xu; G. Hua; M. Hakkarainen; K. Odelius Biomacromolecules 2018, 19, 3077.
2. Y. Xu; K. Odelius; M. Hakkarainen ACS Sustainable Chemistry & Engineering 2019, accepted.

One-Step Synthesis of Biobased Thermoplastic and Thermoset Polyamides with Tuneable Properties

Charalampos Pronoitis, Geng, Hua,
Minna Hakkarainen, Karin Odelius

Department of Fibre
and Polymer Technology,
KTH Royal Institute of Technology,
SE 100-44, Stockholm, Sweden

Polyamides' (PAs) are one of the most useful classes of polymers widely applied in common textiles due to their excellent fiber-forming ability and in advanced applications where high mechanical strength and thermal stability are sought. Their conventional synthesis route involves the polycondensation between diacids and diamines at high temperature and reduced pressure to remove the condensate and also makes use of solvent to prepare the initial corresponding salt. Acyl chlorides may be used instead to perform the reaction at room temperature yet, toxic thionyl chloride is employed and a base is needed to neutralize the acid formed. None of the routes pertains to the principles of green chemistry since both are energy demanding and/or make use of toxic reagents, solvents and auxiliaries and therefore, make the whole process highly unsustainable. In the quest for more sustainable polymers, we developed a completely solvent-free strategy based on the aminolysis of esters which overcomes the aforementioned synthetic downsides and further utilizes ethylene brassylate as monomer which is obtained from renewable resources such as rapeseed oil. Careful selection of the reaction conditions enabled the synthesis of structurally diverse thermoplastic PAs at merely 100 ˚C with varying thermal properties depending on the diamine employed. Further, the PAs exhibited excellent fiber-forming ability.1 Our strategy can be implemented for the synthesis of PA thermosets as well. By altering the stoichiometry of the reaction, materials with tuneable tensile mechanical properties and crosslinking density can be prepared as thin transparent films. Finally, the presence of crystalline regions within the crosslinked polymer network gave rise to a remarkable shape-memory effect.

---

1 Hua, G.; Odelius, K.; Exploiting Ring-Opening Aminolysis-Condensation as a Polymerization Pathway to Structurally Diverse Biobased Polyamides, Biomacromolecules **2018**, 19, 1573-1581

Self-assembly of amphiphilic random copolymers: from single-chain nanostructures to submicron-length scale particles

E. Martinelli, Valentina Gianotti†,‡,
E. Guazzelli, E. Masotti, G. Galli
Department of Chemistry
and Industrial Chemistry,
University of Pisa, 56124 Pisa, Italy

The concept behind the fast developing field of single-chain nanoparticles (SCNPs) is inspired by the precise and efficient folding of natural macromolecules, that can provide complex functions related to their three-dimensional arrangement.[1] The self-assembly of amphiphilic random copolymers consisting of hydrophilic poly(ethylene glycol) methacrylate (PEGMA) and hydrophobic (meth)acrylates is considered one straightforward approach to generate dynamic, stimulus-responsive SCNPs in water, via hydrophobic intramolecular interactions.[2,3] These special SCNPs are generally referred to as unimer micelles, in analogy with the intermolecular micelles formed by common amphiphiles.

In our work we synthesized a set of amphiphilic random copolymers from hydrophilic PEGMA and hydrophobic perfluorohexylethyl acrylate (FA) and polysiloxane methacrylate (SiMA) by controlled radical polymerization and investigated their copolymer-composition dependent self-folded single-chain nanoassemblies in water both experimentally and computationally. DLS measurements on water solutions of the copolymers at room temperature showed the presence of single-chain folded nanoassemblies with hydrodynamic diameter lower than 10 nm. These single-chain assemblies were thermoresponsive and reversibly collapsed into sub-micron multi-chain aggregates at a critical solution temperature. A covalently linked julolidine moiety and an added ethidium bromide were separately used as fluorescent probes to monitor the fluorescence emission of the aggregation state of the copolymers in water solutions.[4] Molecular dynamics simulations revealed the formation of complex prolate single-chain nanoassemblies with a structural variability in water solution.[5] Small angle neutron scattering (SANS) investigations confirmed the self-folded nanoassemblies to be prolate spheroids with a large ratio of polar/equatorial axes (~5:1–~2:1).[6]

---

[1] J.A. Pomposo (Ed.), Single-chain Polymer Nanoparticles: Synthesis, Characterization, Simulations, and Applications, Wiley-VCH, Weinheim, 2017.

[2] T. Terashima, T. Sugita, K. Fukae, M. Sawamoto, Macromolecules, 47 (2014) 589.

[3] Y. Koda, T. Terashima, M. Sawamoto, Macromolecules, 49 (2016) 4534.

[4] E. Martinelli, L. Annunziata, E. Guazzelli, A. Pucci, T. Biver, G. Galli, Macromol. Chem. Phys. 219 (2018) 201800082.

[5] E. Guazzelli, E. Martinelli, G. Galli, L. Cupellini, S. Jurinovich, B. Mennucci, Polymer, 161 (2019) 33.

[6] E. Martinelli, E. Guazzelli, G. Galli, M. T. F. Telling, G. Dal Poggetto, B. Immirzi, F. Domenici, G. Paradossi, Macromol. Chem. Phys., 219 (2018) 201800210.

Nitroxide Mediated Polymerization as New Tool in the Box of Polymeric Deterministic Doping

Riccardo Chiarcos[1,2], Valentina Gianotti[1,2],
Maurizio Cossi[1,2] Alberto Zoccante[1,2],
Diego Antonioli[1,2], Katia Sparnacci[1,2],
Michele Laus[1,2], Michele Perego[3]

1 Dipartimento di Scienze e Innovazione
Tecnologica (DISIT), Universitá del Piemonte
Orientale "A. Avogadro",
Viale T. Michel 11, 115121 Alessandria, Italy

2 INSTM, UdR, Alessandria, Italy

3 Laboratorio MDM, IMM-CNR,
Via C. Olivetti 2, 20864 Agrate Brianza, Italy

An extremely accurate control of the dose and the position of dopant atoms in silicon, named Deterministic Doping, is the necessary condition to ensure the continuous downsizing of electronic devices. Recently our group proposed an innovative technology based on polymers functionalized by a terminal group reactive with the native oxide layer on the silicon substrate and containing a phosphorus atom, the most common n-type dopant1. Exploiting the self-limiting nature of the grafting to reactions, it was demonstrated that it's possible to accurately control the grafting density, and conseguently the amount of phosphorus atoms bonded to the substrate, simply tuning the molecular weight of the polymer chains. A critical point of this technology is the synthesis of the functionalized polymers, made by Atom Transfer Radical Polymerization (ATRP) followed by a phosphorylation reaction. This procedure requires water free enviroment and several purification steps. An easier way to obtain polymers with the above structural features is to use the Nitroxide Mediated Polymerization (NMP) with N-tert-Butyl-N-[1-diethylphosphono(2,2-dimethylpropyl)] Nitroxide (SG1)2 as radical controller. In this work polystyrene samples with molecular weight ranging from 2.5 to 52 kg/mol and narrow molar mass distribution were synthesized using SG1 as radical controller and were grafted onto silicon oxide substrates by Rapid Thermal Processing (RTP) technology3. The thickness of the grafted layer was observed to rapidly increase with annealing time reaching a thickness plateau value, that is significantly lower than the value obtained in the conventional grafting to reactions, when the pseudo-plateau thickness value approach two times the radius of gyration of the corresponding polymer chain. In addition, the plateau thickness increases as the molar mass of the grafting polymer increases for molecular weights lower than 15 kg/mol and then reaches a somewhat limiting thickness, in complete contrast to the classical grafting behavior. Despite this, the phosphorus amount linked to the surface is perfectly equal to the density of the grafted chains estimated from the thickness of the layer. Matching these data with those obtained simulating the grafting to reaction with direct exposure probe analysis4, we concluded that two competing reactions are present during RTP, a grafting reaction and a degradation of the SG1 moiety. The perfect control of the phosphorus amount obtained, suggests this new system as a promising candidate in the Deterministic Doping scene.

Keywords:
(Doping; SG1; Grafting;
Nitroxide Mediated Polymerization)

---

[1] M. Perego, G. Seguini, E. Arduca, A. Nomellini, K. Sparnacci, D. Antonioli, V. Gianotti and M. Laus, ACS Nano, 12, 178–186 (2018).

[2] S. Grimaldi, J. Finet, L. Moigne, A. Zeghdaoui, P. Tordo, D. Benoit, M. Fontanille and Y. Gnanou, Macromolecules, 33, 1141-1147 (2000).

[3] F. Ferrarese Lupi, T. J. Giammaria, G. Seguini, M. Ceresoli, M. Perego, D. Antonioli, V. Gianotti, K. Sparnacci and M. Laus, J. Mater. Chem. C, 2, 4909-4917 (2014).

[4] M. Ceresoli, F. Ferrarese Lupi, G. Seguini, K. Sparnacci, V. Gianotti, D. Antonioli, M. Laus, L. Boarino and M. Perego, Nanotechnology, 25, 275601 (2014).

Sequential infiltration synthesis in block copolymers films: quantitative analysis by reference-free grazing-incidence X-ray fluorescence

Eleonora Cara[1, 3*], Federico Ferrarese Lupi[1],
Philipp Hönicke[2], Yves Kayser[2], Samuele Porro[3],
Fabrizio Pirri[3], Burkhard Beckhoff[2],
Natascia De Leo[1], Luca Boarino[1]

1 Advanced Materials and Life Science Division,
Istituto Nazionale Ricerca Metrologica, Strada
delle Cacce 91, 10135 Torino, Italy

2 Physikalisch-Technische Bundesanstalt (PTB),
Abbestr. 2-12, 10587 Berlin, Germany

3 Dipartimento di Scienza Applicata
e Tecnologia, Politecnico di Torino,
Corso Duca degli Abruzzi, 24, Torino, Italy

* e.cara@inrim.it

Sequential infiltration synthesis (SIS) [1] is a technique derived from atomic layer deposition (ALD) and consists in the cyclic infiltration of a polymer with inorganic compounds through the sequential and self-limiting exposure to gaseous precursors. Such technique is used to harden polymeric lithographic masks with low etching resistance in order to give access to high aspect ratio pattern transfer in the dimensional range below 20 nm, as required by many fabrication processes including nanoelectronic circuit. SIS applications also include the manipulation of refractive index for surface coatings [2] and the realisation of complex inorganic nanostructures in block copolymers (BCPs) templates [3]. In common PS-b-PMMA BCPs systems, Al_2O_3 can be grown by cyclic reactions of trimethyl-aluminum (TMA) and H_2O and its infiltration occurs selectively in PMMA nanodomains due to their chemical affinity to TMA. Despite its broad use, the mechanism of the infiltration in polymeric systems is still debated and the role of polystyrene as a diffusion channel has been proposed [4]. A better understanding of the infiltration process can be achieved by means of grazing-incidence X-ray fluorescence (GIXRF). The depth-dependent nature of GIXRF and the employment of radiometrically calibrated instrumentation at PTB beamline at BESSY II electron storage ring allow for an in-depth absolute quantification of the infiltrated oxide without any reference material [5,6].

Reference-free GIXRF analysis was performed on a layer of PMMA resist for electron beam nanolithography (EBL), PSr-PMMA and PS-b-PMMA layers treated with 1 to 10 cycles of Al2O3 ALD to obtain the absolute quantification of the aluminum mass deposition and the analysis of the infiltration depth profile.and believe that these sensors could tackle the lack of methods for the real-time quali-quantitative air monitoring in urban and industrial environments, which currently requires long-time sampling, separation processes and laboratory analyses.7 We also believe that, thanks to the ease of mass-scale fabrication of polymer DBRs and their ease of integration with packaging technologies,8 this method will be industrially relevant for the in-situ assessment of diffusive processes of degradation by-products, humidity or even oxygen in smart packaging systems for foods and optoelectronic devices.

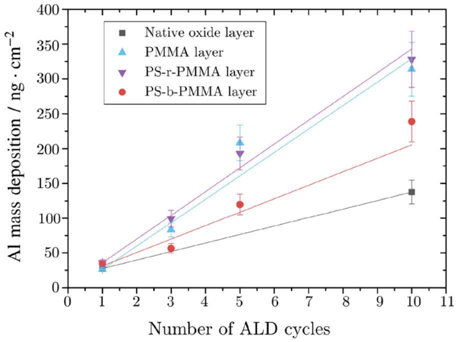


Figure 1:
Scatter plot
of the mass
of aluminum
per unit area
infiltrated in the
four different
samples set as a
function of the
number of
ALD cycles

---

1 Y. C. Tseng, et al., J. Mater. Chem, 21, 2011, 11722. 2 D. Berman, et al., ACS Nano, 11, 3, 2017, 2521. 3 J. Kamcev, et al., ACS Nano, 7, 2012, 339. 4 M. Biswas, et al., J. Phys. Chem. C, 119, 2015, 14585.
5 M. Müller, et al., Materials, 7(4), 2014, 3147. 6 P. Hönicke, et al., Phys. Status Solidi A, 212 (3), 2015, 523.

Viscosity scaling factors for different polysaccharides in salt-free solutions

A. Dodero[1], M. Alloisio[1], S. Vicini[1], S. Gagliardi[2],
R. Williams[3], M. Castellano[1]
andrea.dodero@edu.unige.it

1 University of Genoa,
Department of Chemistry
and Industrial Chemistry,
Via Dodecaneso 31, 16146 Genoa (Italy)

2 Edinburgh Napier University,
School of Engineering
& the Built Environment, Colinton Road 10,
EH10 5DT Edinburgh (Scotland)

3 The University of Edinburgh,
School of Engineering,
Robert Stevenson Road,
EH9 3FD, Edinburgh (Scotland)

Polysaccharides represent an important class of natural occurring biopolymers nowadays widely used for several purposes, ranging from biomedical to water treatments applications. Most polysaccharides are characterized by the presence of positive or negative charges on the backbone of the polymer chains, which strongly influence their behaviour in solutions compared to neutral polymers. The most evident effects can be observed studying the concentration regimes and the related concentration dependence of the solution viscosity[1].

In the present work, the polyelectrolyte nature of alginate, chitosan and hyaluronic acid was investigated in deionized water via rheological measurements; plotting the experimental specific viscosity data as a function of the solution concentration, the viscosity scaling factors α (representing the viscosity concentration dependence) and the critical concentrations (separating the dilute, the semi-dilute unentangled, the semi-dilute entangled, and the concentrated regimes) were evaluated applying a power law regression[2] ($\eta_{sp} \infty c^{\alpha}$).

All the studied materials showed scaling factors in line with those reported in literature, thus confirming their polyelectrolyte nature; indeed, such polymers are characterized by lower scaling factors compared to neutral polymers due to the rigid “rod-like” chain conformation, which reduce the number of entanglements in solution[3]. Moreover, some interesting differences were obtained for the three polysaccharides suggesting that the molecular structure plays an important role in conditioning their behaviour. In particular, the presence of sterically hindered side groups on chitosan chains reduced the entanglement formation leading to a further lower viscosity concentration dependence.

---

[1] Dodero, A.; Vicini, S.; Alloisio, M.; Castellano, M. Sodium Alginate Solutions: Correlation between Rheological Properties and Spinnability. J. Mater. Sci. **2019**, 54 (10), 8034–8046. https://doi.org/10.1007/s10853-019-03446-3.

[2] Colby, R. H. Structure and Linear Viscoelasticity of Flexible Polymer Solutions: Comparison of Polyelectrolyte and Neutral Polymer Solutions. Rheol. Acta **2010**, 49 (5), 425–442. https://doi.org/10.1007/s00397-009-0413-5.

[3] Dobrynin, A. V.; Colby, R. H.; Rubinstein, M. Scaling Theory of Polyelectrolyte Solutions. Macromolecules **1995**, 28 (6), 1859–1871. https://doi.org/10.1021/ma00110a021.

Directed Self-Assembly of Block Copolymer/Homopolymer Blends

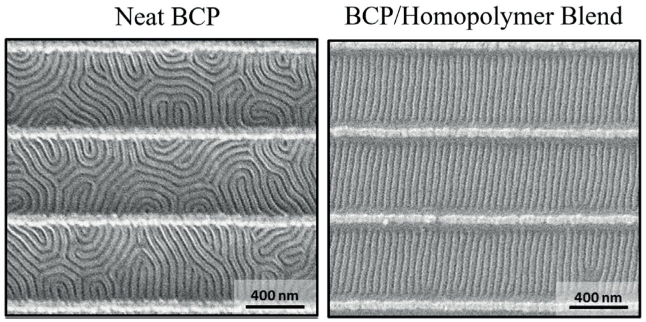
I. Murataj[1-2], F. Ferrarese Lupi[1], A. Angelini[1-2], F. Frascella[2], R. Chiarcos[3], D. Antonioli[3], V. Gianotti[3], N. De Leo[1], F. Pirri[2], L. Boarino[1], M. Laus[3]

1 Nanoscience and Materials Division,
Istituto Nazionale Ricerca Metrologica,
Strada delle Cacce 91, 10135 Torino, Italy

2 Dipartimento di Scienza Applicata
e Tecnologia, Politecnico di Torino,
Corso Duca degli Abruzzi 24, Torino, Italy

3 Dipartimento di Scienze e Innovazione
Tecnologica (DISIT), Università del
Piemonte Orientale "A. Avogadro",
Viale T. Michel 11, 15121 Alessandria, Italy

The practical implementation of block copolymers in nanolithography requires the enhancement of the lateral ordering of the nano-domains. To this goal, the use of BCP/homopolymer ternary blends has been proposed in order to sensibly increase the grain size of nanometric structures [1]. Here, we investigate the long-range ordering (ξ) of lamellae-forming poly(styrene-block-methyl methacrylate) (PS-*b*-PMMA) BCP when blended with constituent low molecular weight (Mn) homopolymers PS and PMMA (~ 3 kg/mol). At high temperature annealing treatments (210 °C ≤ T_a ≤ 330 °C) the BCP/homopolymer ternary blends undergo to a fast degradation, resulting in a 20 °C decrease of the stability temperature respect to the unblended BCP that leads to a sensible reduction of the processing window available for the formation of a flat homogeneous film. However, the introduction of homopolymers brings to one order of magnitude increase in the lateral ordering (ξ_{blend} ~ 1300 nm) if compared to the neat BCP (ξ_{neat} ~ 140 nm). The lithographic suitability of BCP/homopolymer ternary blends is demonstrated by the self-assembly process inside grapho-epitaxial defined linear trenches. Moreover, the inhomogeneous films revealed the formation of dewetted droplets randomly disposed on the substrate and composed by a discrete number of orderly arranged lamellae propagating for distances far exceeding the ordering on flat substrates.



SEM micrographs describing the BCP ordering on of "neat" and "blended" BCP inside HSQ trenches.

---

[1] Gregory S. Doerk, Kevin G. Yager, "Rapid Ordering in "Wet Brush" Block Copolymer/Homopolymer Ternary Blends" ACS Nano 2017, 11, 12326–12336.