

Research Networking Programme

Precision Polymer Materials (P2M)

Standing Committee for Physical and Engineering Sciences (PESC)

The aim of the European Science Foundation (ESF) Research Networking Programme P2M is to combine the complementary expertise of leading European research groups in the design of **precision polymeric materials**, i.e., polymers with precisely defined molecular weight, architecture and functionality that are designed to self-assemble into functional materials via strategies that are **inspired by or mimic biological self-assembly processes**. The main aim of the programme is to promote interactions and facilitate the exchange of, primarily, early career researchers with different backgrounds, ranging from **catalysis, polymer chemistry and physics to theory, biochemistry and pharmacy**.

A central part of the research programme concerns the design of multifunctional polymer nano-edifices. By learning from the principles used in nature to achieve responsive, dynamic, active materials, it is possible to utilise synthetic or biological polymer systems to design active biomaterials. Such a biomimetic approach can have considerable impact, not only for biomedical applications, but also in the design of **functional nanomaterials**.

The overall goal of P2M will be the advancement of fundamental knowledge in polymer science and engineering beyond the state of the art: more specifically, the design and synthesis – through sustainable polymer chemistry methodologies – of new functional polymers with self-assembling and/or templating properties towards nanostructured materials, material systems and devices using simple processing methods. The ultimate goal is to design new functional polymer materials and processes for future information and communication, energy, life science and environmental technologies as well as to **train highly skilled people who will be joining either academia, traditional and high technology industries** or will be contributing to creating new high tech industrial sectors.

A major aim of the P2M programme will be the training of young researchers, who will benefit from the fruitful exchanges of knowledge and expertise occurring between the participating groups. In order to illustrate this integrated approach, some examples of research topics that will be investigated within the P2M Programme are described below. Three different objectives can be emphasised: **precision polymer synthesis, controlled and directed self-assembly and (multi)functional polymer materials**.

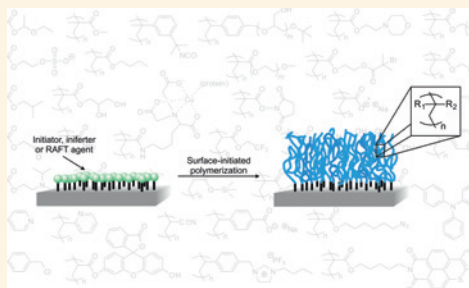
The groups involved have great experience in the synthesis, characterisation and modelling of complex and functional polymer systems, allowing synergy for the elaboration and optimisation of novel bio-inspired and functional materials with fine-tuned properties and for their future industrial application.

The running period of the ESF Research Networking Programme P2M is for four years, from **April 2011 to April 2015**.

Scientific Context and Challenges

The 20th century polymer industry mainly resorted to monomers arising from petroleum-based products. This has led to the development of polymeric materials that are well positioned in many key aspects of our daily-life. The controlled design, precision synthesis and characterisation allow fine control of the self-organisation of polymer materials on different length scales and are the key technology for today and tomorrow. As a result, block copolymer materials are widely used in industry as thermoplastic elastomers, reinforcement materials, adhesives, but also as scaffold or template for microelectronics. Their ability to self-assemble in bulk and in solution into well-defined and predictable nanostructures also opened avenues in drug delivery systems, biosensors or electronic devices. The thorough understanding of the self-organising processes as well as the understanding and the precise control of structure and function on multiple length scales will be essential prerequisites for any significant progress. However, there is a critical need to diminish our reliance on fossil resources and to invent new polymer systems that respond to the needs of our modern societies.

Figure 1. Synthesis of polymer brushes via surface-initiated controlled radical polymerisation (kindly provided by Harm-Anton Klok, EPFL, Switzerland)



Precision Polymer Synthesis

New approaches in polymerisation catalysis

A striking observation is the extreme diversity of metallic catalytic systems employed in polymer synthesis. In most cases, the metallic catalyst represents minute amounts and yet remains in the final polymer. In sensitive domains such as biomedical, packaging and microelectronics, metal-based catalysts are prohibited. Organic and enzymatic catalysis appear today as the most reliable alternatives to metal-mediated catalysis for polymer synthesis. Organic and enzymatic catalysts can be designed to break down into innocuous products at the end of their functional use. New concerns for the coming years are thus to implement sustainable routes to polymers by using either bio-inspired, organo-catalytic platforms and/or modified enzymes, or single organic catalysts such as *N*-heterocyclic carbenes (NHCs). These three families of catalysts have already proved their effectiveness in some key polymerisation reactions. A particular aim will be to develop multi-task catalytic platforms.

Controlled polymerisations for defined polymeric architectures

Polymerisation techniques allowing perfect control of the macromolecular parameters (molecular weight, stereo-regularity, location of functional groups, etc.) and architectures (block, star-like, comb-like, dendrimer-like and hyperbranched polymers) are needed to obtain some of the starting materials that will be further used in the P2M programme. Typical examples are living anionic and controlled radical polymerisation techniques that are commonly used by several partners of the programme. Additional synthetic tools such as the popular “click”-chemistry

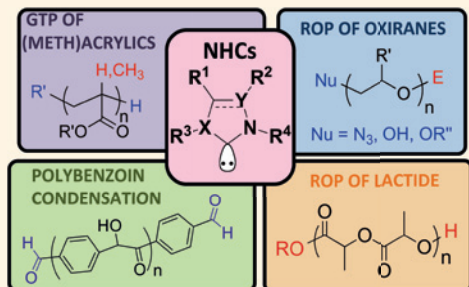


Figure 2. Examples of metal-free precise polymer synthesis employing N-heterocyclic carbenes as organic catalysts both ion chain-growth and step-growth polymerisation reactions. (kindly provided by Daniel Taton, LCPO-ENSCBP, Université de Bordeaux, France)

approach will also be used in order to add specific functional groups or to create macromolecules with complex topologies. Emphasis will be put on the introduction of functional groups at precise locations in the resulting polymer chains. Such functional groups will allow specific motives to be introduced for further supramolecular secondary interactions (e.g. hydrogen-bonding or metal-ligand interactions), following a protein-mimicking approach.

Hybrid polymer-biological polymer systems

The synthesis of well-defined biological – synthetic polymer conjugates is an important area of research given the potential of the resulting materials for a broad range of applications. In spite of the vast interest in these materials, however, the synthesis of well-defined peptide/-protein-polymer conjugates, i.e., hybrid constructs which combine (i) a defined number of peptide/protein segments with uniform chain lengths and defined monomer sequences (primary structure) with (ii) a defined number of synthetic polymer chains, is still a challenge. The

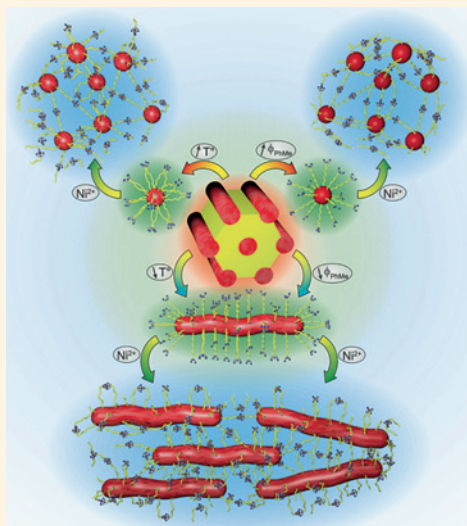


Figure 3. Smart micellar gels with tunable properties based on metal-ligand complexes. (kindly provided by Jean-François Gohy, Université Catholique de Louvain, Belgium)

three main strategies that are currently used for the preparation of peptide/protein synthetic polymer conjugates, (i) α -amino acid N-carboxyanhydride (NCA) ring-opening polymerisation, (ii) solid phase peptide synthesis (SPPS) and (iii) protein biosynthesis, each have their limitations and drawbacks and there is a clear need for improved methodologies to synthesise biological-synthetic hybrid constructs with enhanced control over the conjugation site and the number of attached polymer chains.

Controlled and Directed Self-Assembly

The driving idea is to combine block copolymer self-assembly, mainly driven by the chemical incompatibility between both blocks and the entropy minimisation of the resultant structure, with other controlled and precise interactions, mainly coming from supramolecular chemistry (H-bonding, metal complexation, secondary structure, chirality, etc.) and biology (peptide, protein and DNA building blocks).

Self-assembly via supramolecular interactions

Self-recognition and self-assembly are the two pillars on which supramolecular chemistry is based, involving mainly interactions of non-covalent nature (van der Waals, hydrogen bonding, coordinative interactions, etc.). The large range of interaction strength, directionality, and reversibility offered by these interactions allows unprecedented control over the structure and properties of materials, enabling the synthesis of large and complex structures with diverse functions interesting for many different fields. Such approaches should lead to systems combining the characteristic features of block copolymers (e.g., microphase

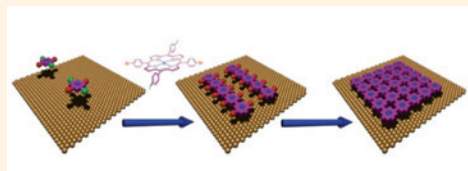


Figure 4. 2D Polymers by Sequential Growth: Custom-designed monomers equipped with two different activating groups polymerise first (at low temperature) in one dimension to yield chains, which are then (at higher temperature) crosslinked in the second dimension. (kindly provided by Stefan Hecht, Humboldt University, Berlin, Germany)

separation between immiscible constituent blocks) with those of supramolecular polymers (e.g., reversibility and tunability of the strength of the supramolecular bonds). The supramolecular linkers can be used to either bridge together different homopolymer blocks, or to link together different block copolymers. Such systems will be studied thoroughly by several partners of this programme.

Peptide- and protein-based self-assemblies

Peptide/protein – synthetic polymer conjugates, which covalently combine one or more copies of a peptide sequence or protein with one or more synthetic polymer elements offer unique possibilities to integrate the properties and functions of bio(macro)molecules and synthetic polymers in a single hybrid material. Peptide-synthetic polymer conjugates, for example, are of interest for drug and gene delivery, as structural materials and hydrogels and to direct mineralisation. Covalently combining proteins and synthetic polymers is of interest for numerous reasons. The conjugation of an appropriate synthetic polymer can be used, for example, to modulate the biological activity of a protein. From the polymer perspective, the attachment of a protein may endow a synthetic polymer with unique functional and structural properties.

DNA-based self-assemblies

The use of DNA to build up 2D and 3D nanostructures is based on the unique and reversible recognition properties of oligonucleotides (ODN), and interest in such applications has increased in recent years. Nowadays, the DNA-based technologies have reached a certain maturity and the elaboration of DNA-based block copolymers can be envisaged. As for peptide- or protein- based self-assemblies,

DNA-based technologies aim to combine a precisely controlled self-assembly process together with a predefined biofunctionality. This would open a new field of interdisciplinary research, at the interface between polymer chemistry, biology and nanoscience.

(Multi)Functional Polymer Materials **Drug delivery systems**

New advances in drug design and delivery, systems biology, and more generally in nanomedicine ensure that the potential of polymer science and technology to improve health care is stronger than ever. Recent developments in synthetic methods have allowed the design of sophisticated polymers and block copolymers based on biodegradable or highly biocompatible segments. Although progress has been made in polymeric biomaterials, several challenges exist in the implementation of such materials as medical tools or applications. A key barrier is the difficulty of directly correlating structure-property relationships with cellular function. An additional challenge in drug delivery includes the delivery of sensitive biological drugs such as proteins, antibodies or Si-RNA, which are highly sensitive to process conditions due to their tendency to denature. Another recent domain consists in the design of multifunctional drug-delivery systems, able to load a large amount of therapeutic molecule, to release its content in a spatial and temporal controlled manner, and with the capability to serve as a contrast agent for magnetic resonance imaging or other imaging methods. The main challenge of the coming decade is to move from the current use of polymer materials in a 'passive' way to an 'active' one, where the polymer itself will have a functional role.

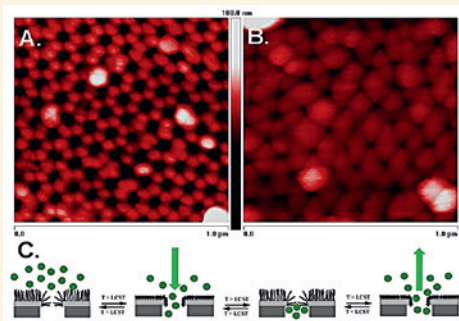


Figure 5. AFM images showing (A) 2D platform of nanocontainers made of anodised aluminium oxide and (B) the same sample gated with grafted thermoresponsive PNIPAM brushes. The diagram underneath shows the loading and releasing mechanism of the nanocontainers controlled by the polymeric brush nanovalves (kindly provided by Szczepan Zapotoczny, Jagiellonian University, Poland)

Surface active materials

The development of materials with intelligent surface properties, e.g. sensing properties, ultrahydrophobicity and switchable wettability is of great importance for many micro- and nanotechnological applications. Using both grafting-onto (chemi- and physi-sorption) as well as grafting-from strategies (surface-initiated polymerisation), the activities in the framework of this programme will aim to use the latest synthetic advances and state-of-the-art micro/nanolithographic tools to generate thin polymer coatings that are molecularly defined with respect to chemical composition and architecture and have properties that are fine-tuned for a range of applications varying from biomaterials coatings, to microfluidics and sensors.

Nanoreactors

The ability of (functional) block copolymers to self-assemble into nanodomains of precise shape, size and chemical

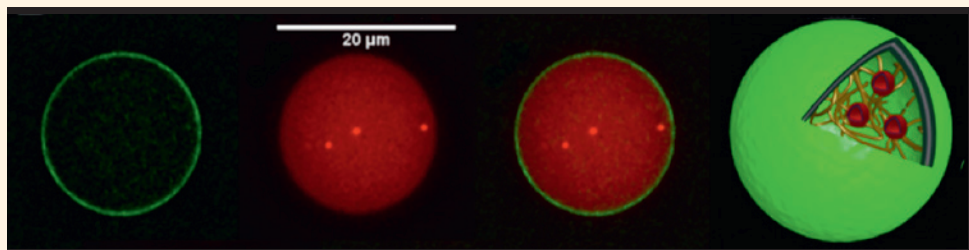


Figure 6. An example of compartmentalised polymersomes obtained from emulsion/centrifugation methods that mimic the cellular structure. (kindly provided by Sébastien Lecommandoux, LCPO-ENSCBP, Université de Bordeaux, France)

environment is a key feature allowing a possible use of these systems as nanoreactors. The cell, its structure and mechanisms, is certainly one of the most complex, and exciting systems that scientists are still trying to recreate/mimic and fully understand. The first and foremost challenge in order to obtain cell mimics lies in the controlled formation of such complex structures which although non-living, will roughly approach the complexity and functionality of living cells. Once the generation of these mimics is controlled and optimised, material scientists should be able to take advantage of their structure to gain new properties and form completely innovative, with previously unmatched efficiency, soft biomimetic materials.

Bio-electronic polymer materials

The coupling of electronics with living tissue holds the key to a variety of important life-enhancing technologies and still represents a very challenging area for the future. One example is bio-electronic implants that record neural signals and/or electrically stimulate neurons. These devices offer unique opportunities to understand and treat conditions such as hearing and vision loss, epilepsy, brain degenerative

diseases, and spinal cord injury. Another example is sensor arrays that utilise living cells as the bio-recognition element. These devices offer tremendous value in new drug development and in detectors/sensors protecting human and animal health and the environment. Key to these technologies is a fundamental understanding of electrical communication at the interface between electronic materials and living cells. Improved understanding of this interface will translate to implants that are more stable and dissipate less power, and sensors that offer better sensitivity and lower detection limits, both unresolved and pressing needs in the field.

Scientific Activities

Workshops and conferences

The Steering Committee organises international workshops with around 50 participants which are held about once a year. The main contributors to the P2M programme will discuss the advancement of common research during this annual meeting. In addition larger international conferences with around 100 participants will be organised every two years and will cover a broader range of people.

Between the conferences and workshops, the supervision will be organised by members of the P2M Steering Committee. Connection between different teams both at a national and international level will be organised using telecommunication including organisation of teleconferences.

Exchange visit grants

These are mainly for young scientists who need further training and expertise in new experimental and modelling methods for a fruitful continuation and broadening of their research scopes. These grants are intended to facilitate the transfer of knowledge and techniques relevant to research from one laboratory to another within Europe (at least one contributing country should be involved). The grants are for periods up to six months.

Short visit grants

These cover the costs of short visits of senior researchers working in the area of the P2M programme, in order to carry out joint work primarily in one of the STIPOMAT (Experimental and Theoretical Design of Stimuli-Responsive Polymeric Materials) participating laboratories.

The online applications are accessible on www.esf.org/p2m

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Cover picture:

Precision polymer design can exquisitely control materials properties.

(from LCPO-CNRS, Université de Bordeaux)

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