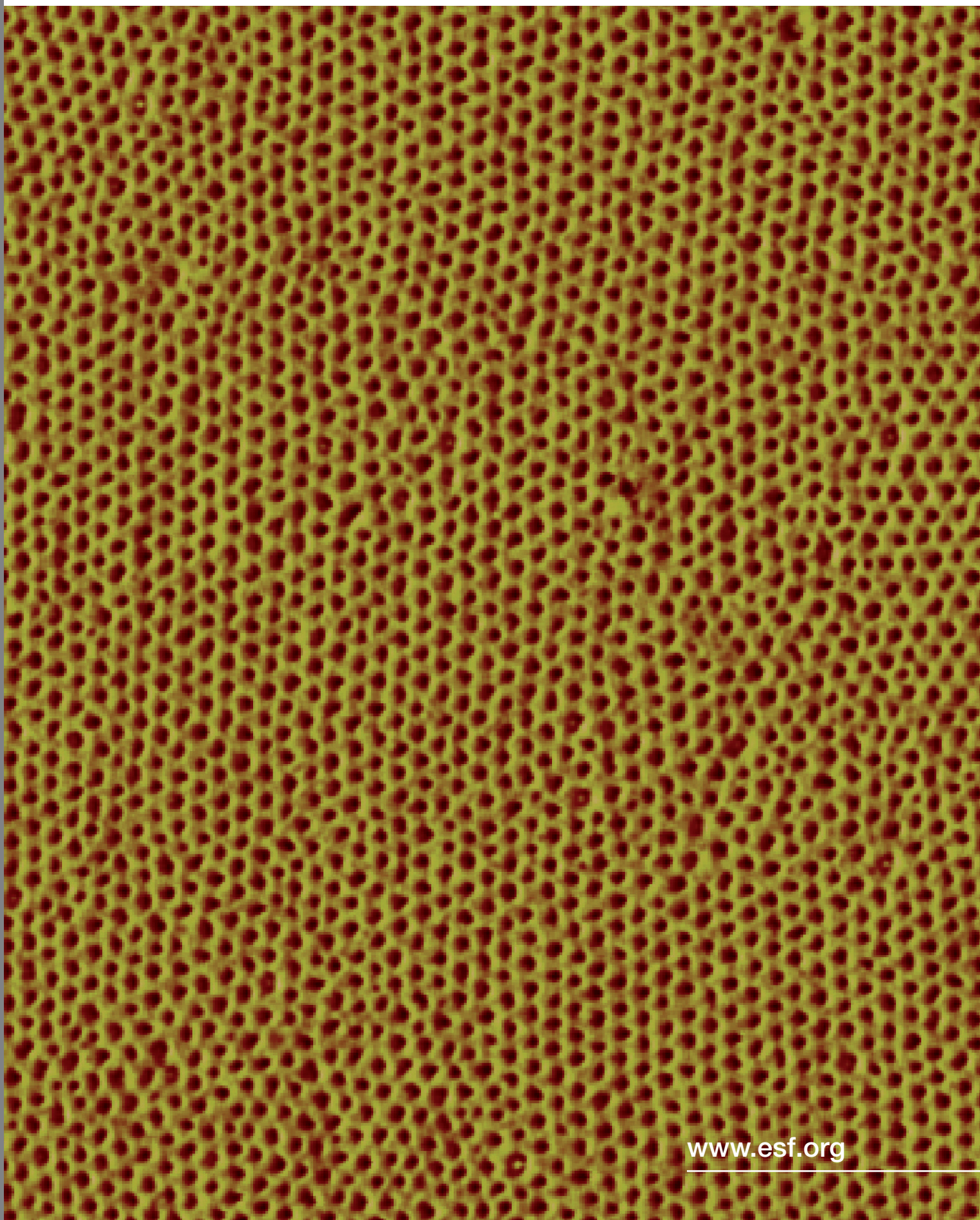
EUROPEAN SCIENCE FOUNDATION

SETTING SCIENCE AGENDAS FOR EUROPE

RESEARCH NETWORKING PROGRAMME

EXPERIMENTAL AND THEORETICAL DESIGN OF STIMULI-RESPONSIVE POLYMERIC MATERIALS (STIPOMAT)

Standing Committee for Physical and Engineering Sciences (PESC)



www.esf.org

The European Science Foundation (ESF) was established in 1974 to create a common European platform for cross-border cooperation in all aspects of scientific research.

With its emphasis on a multidisciplinary and pan-European approach, the Foundation provides the leadership necessary to open new frontiers in European science.

Its activities include providing science policy advice (Science Strategy); stimulating co-operation between researchers and organisations to explore new directions (Science Synergy); and the administration of externally funded programmes (Science Management). These take place in the following areas: Physical and engineering sciences; Medical sciences; Life, earth and environmental sciences; Humanities; Social sciences; Polar; Marine; Space; Radio astronomy frequencies; Nuclear physics.

Headquartered in Strasbourg with offices in Brussels, the ESF's membership comprises 76 national funding agencies, research-performing agencies and academies from 30 European nations.

The Foundation's independence allows the ESF to objectively represent the priorities of all these members.

Introduction

The aim of the STIPOMAT Programme is to combine the complementary expertise of European research groups in the experimental and theoretical study of complex structures on the basis of stimuli-responsive polymers and copolymers with linear or complex topology in order to gain a deeper understanding of two fundamental aspects of polymer science.

The first question is the understanding of the formation of such structures: self-assembly in stimuli-responsive block copolymers, dendrimers, branched polymers, thermo-responsive gels, interpolymer supramolecular complexes, networks with varying topologies and hybrids of responsive polymers with biopolymers.

The second question is the correlation between the behaviour of these polymer systems under the change of external conditions (temperature, pressure, electric or magnetic field, shear, ionic strength, pH and composition of solution, etc). and the chemical structure of the constituents.

The research project will involve elaboration of new stimuli-responsive polymeric materials, application of advanced experimental methods in addition to atomistic and coarse-grained modelling, molecular mechanics, molecular dynamics and stochastic methods to determine structure and dynamical properties under different external conditions as well as kinetics of structure transformation of such systems under external stimuli. The groups involved have great experience in the synthesis, characterisation, modelling and theory of complex polymer systems.
The unique combination of synthesis, characterisation, theory and modelling will allow a synergy for the elaboration and optimisation of novel multi-responsive materials with fine-tuned properties and for their future application in industry.

In chemistry, the last few years have led to the development of new interdisciplinary branches combining and bridging different fields. The building principles and the perfect structures found in nature have served as motivation and as models. The combined efforts have led to compounds with ordered architectures. The design, synthesis, characterisation and controlled self-organisation of the required well-defined materials and systems on different length scales will be the key technology for the next decade. The results obtained up to now are just the very beginning of this development. The next years will be dedicated to further bridging the gap between synthetic and natural systems.

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. Complex polymer structures combining different polymeric blocks into various topologies are an important part of this effort.

The realisation of the final structure uses the contribution of different interactions: hydrogen-bonding, Van der Waals interactions, ionic interactions, metal-ligand interactions, hydrophobic interactions and entropic contributions. The chains and chain-segments gain, through these interactions, the possibility of recognising binding partners within and outside their own chains and to realise a final ordered structure. Such interactions are known to be sensitive to macroscopic boundary conditions (environmental changes) through the modulation of their strength and directionality. These systems can therefore serve as stimuli-responsive intelligent materials whose properties can be reversibly fine-tuned in the presence of the appropriate stimulus. This situation is reminiscent of biological systems in which such an approach is systematically used in order to infer a specific function to a structural unit.

The running period of the ESF STIPOMAT Research Networking Programme is for four years from April 2005 to April 2009.

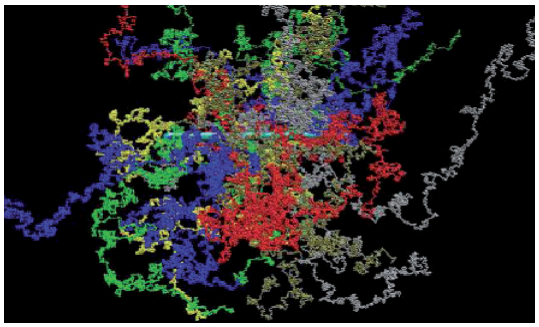
Framework of the scientific programme

Stimuli-responsive polymeric systems show a strong response to external stimuli (which result in forces on monomeric groups that normally are much weaker than typical intermolecular forces) only if there is a delicate balance between different types of interaction present in the system. It is clear that a search for suitable systems via suitable 'chemical design' and appropriate sophisticated chemical synthesis techniques will greatly benefit from theoretical guidance coming from a theoretical analysis (by both analytical techniques and computer simulation) of suitable model systems.

In the STIPOMAT Programme, we would like to study stimuli-responsive complex polymer structures. Such polymers with new functionalities are expected to be applied in novel high technology applications, e.g. for a new class of sensors and to mimic, to some extent, biological systems.

The Programme will be based on an interdisciplinary approach merging research teams involved in the synthesis of stimuli-responsive complex polymer structures, in the characterisation of these systems on both the microscopic and macroscopic level and in theory and simulation. Such a unique combination of expertise is expected to lead to a dramatic increase in the understanding of complex structures. A major concern in the Programme will be the training of young researchers, who will benefit from the fruitful exchange of knowledge and expertise between the participating groups.

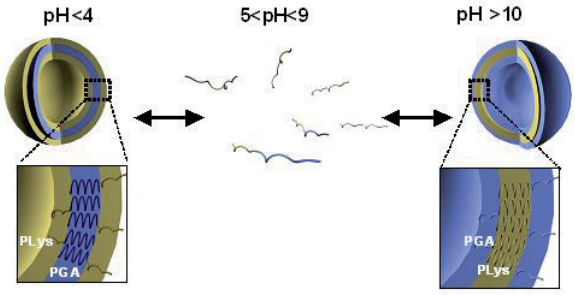
An example of a complex polymer structure investigated in STIPOMAT: a 3d bottle-brush with 64 128 monomers on a simple cubic lattice in a good solvent. The bottle-brush consists of 128 monomers on a rigid backbone, 2 000 monomers on each side chain, and in total 32 side chains grafted to the backbone with equal distance
(kindly provided by Kurt Binder and Hsiao-Ping Hsu from the University of Mainz).



The need for complex macromolecular structures with controlled architectures

The STIPOMAT Programme involves the synthesis of stimuli-responsive polymers and their copolymers with linear or complex topologies. Therefore, living and controlled polymerisation techniques allowing a perfect control of the macromolecular parameters (molecular weight, stereo-regularity, location of functional groups, etc.) and topology (block, dendritic and hyperbranched polymers as well as interpenetrating and semi-interpenetrating networks) are typically used in the STIPOMAT Programme. Special emphasis is devoted to the application of these techniques for the synthesis of stimuli-responsive water-soluble polymer blocks such as poly(2-vinylpyridine), poly(methacrylic acid), poly(ethylene oxide), poly(vinyl ethers), poly(N-alkylacrylamide), poly(N-vinyl caprolactam) and polypeptides that exhibit pH, ionic strength or temperature-dependent behaviour and that will be combined together or with other hydrophobic blocks. The topology of the resulting block copolymer (linear, comb-like, hyperbranched, star-like, networks) is also systematically varied in the targeted complex polymer structures. Special techniques such as solid-phase synthesis are also implemented for the preparation of polypeptides that will then be coupled to well-defined synthetic polymers.
Other stimuli-responsive polymeric materials are obtained in this Programme by combining conducting polymers to an interpenetrating network in order to build electrically responsive actuators or artificial muscles.

An example of a pH-responsive polypeptide-containing polymer: schematic representation of the reversible self-assembly into vesicles of a pH-responsive poly(L-glutamic acid)-b-poly(L-lysine) PGA-b-PLys diblock copolymer
(kindly provided by Sébastien Lecommandoux, LCPO, ENSCPB, Université Bordeaux 1).

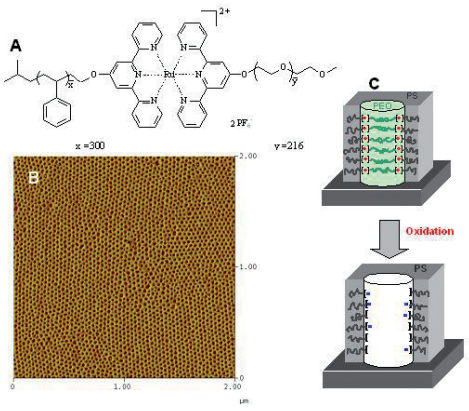


The need for complex macromolecular structures with controlled architectures

Supramolecular chemistry is used in the STIPOMAT Programme to assemble different polymer blocks functionalised by suitable ligands. In this respect, terpyridine-ruthenium complexes are promising candidates for the formation of the so-called metallo-supramolecular copolymers. In this novel synthetic approach, a polymer A block is functionalised with terpyridine ligands whose position in the polymer chain is controlled (at one end, on both ends, along the backbone). Mono-terpyridine-ruthenium complexes can then be selectively formed by complexation of terpyridine with Ru(III). These mono-complexes are then further reacted with other terpyridine-functionalised polymer B blocks while Ru(III) is reduced to Ru(II). This results in bis-terpyridine-ruthenium complexes which act as non-covalent linkages between the polymer A and B blocks. The resulting metallo-supramolecular A-[Ru]-B block copolymers are quite stable and do not show ligand exchange over very long time-scales (years), they can be manipulated as block copolymers and self-assembled. However, under specific conditions, the complexes can be opened-up, which opens new avenues for the application of such polymeric materials. Moreover, these 'lego'-type clicking units can serve as building blocks towards complex copolymer topologies. These metallo-supramolecular copolymers are thoroughly investigated in the frame of the STIPOMAT Programme.

The formation of a nanoporous functional thin film from a metallo-supramolecular block copolymer:the chemical structure of the copolymer (A); a phase-contrast AFM picture of the thin film obtained from this copolymer and showing an array of perpendicular cylinders (B) and a schematic representation of the oxidation process of the metal ions leading to the opening of the complexes and to a nanoporous thin film after removal of the PEO minor blocks (C)

(kindly provided from Jean-François Gohy and Charles-André Fustin, CMAT, Université catholique de Louvain).

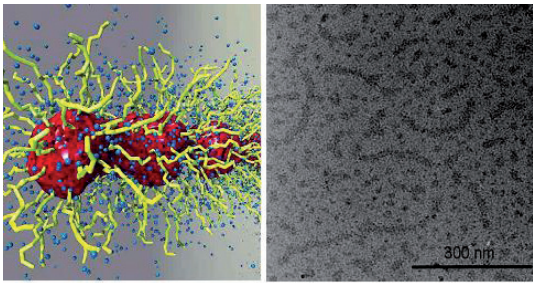


Characterising stimuli-responsive complex polymer structures

The self-assembly of the stimuli-responsive complex polymer structures is controlled by introducing supramolecular non-covalent interactions between specific polymer segments or blocks, resulting in complex polymeric superstructures. The primary structure and topology of the copolymer determine the location of such non-covalent interactions and hence the secondary (or even tertiary) structure of the super-aggregates. The properties of the polymer blocks and segments as well as the supramolecular interactions are then fine-tuned by the application of external stimuli. The understanding of the self-assembly process as well as the response of the accordingly obtained superstructures towards external stimuli require appropriate characterisation tools.

An example of an interdisplinary research project conducted in STIPOMAT. Left image: a snapshot of simulation for worm-like aggregates formed by a four-arm poly(methylmethacrylate)-block-poly (acrylic acid) star block copolymer. Right image: an experimental cryo-TEM picture of the same system

(kindly provided by Heikki Tenhu, Anna Zarembo and Satu Strandman from the University of Helsinki).



Advanced spectroscopic, scattering, microscopy and calorimetric methods are available within the network. Application of NMR relaxation methods, ultrasonic and dielectric relaxation methods, measurements of rheological and mechanical properties, neutron, X-ray and laser light-scattering analysis, scanning and transmission electron microscopy techniques for morphological characterisation and scanning probe microscopies form the basis of the experimental work on characterising complex polymer structures. The stimuli-responsive polymeric materials prepared in the frame of STIPOMAT are thoroughly characterised by using the pertinent techniques.

The need for theoretical approaches

The experience of all participating groups in the preparation and characterisation as well as in the theoretical description of polymer systems are combined to develop novel approaches for the optimised synthesis of stimuli-responsive complex polymer structures. An integrated approach is used in which characterisation, theory and simulation efforts will be devoted to selected stimuli-responsive complex polymer systems. The feedback from the theory and simulation is then used in order to optimise the design of the complex polymer structures.

An essential aspect of the theoretical modelling required for these types of materials is the multiscale character of the problem. An atomistic description must include input from quantum chemistry (for the description of intra-chain potentials) and Car-Parrinello-type 'ab initio molecular dynamics' methods, for instance. Some of the groups included in the STIPOMAT network bring excellence and experience to both the special multiscale coarse-grained techniques and the more standard classical Molecular Dynamics and Monte Carlo simulations. More detailed ab initio simulation on the base of Density functional theory, DFT, are also applied.

A particularly intriguing problem occurs for water-soluble polymers (e.g. biopolymers and synthetic polyelectrolytes) where protonated water cluster H+ • (H2O)n plays a role. In this case, the formation and breaking of the network of hydrogen bonds has to be taken into account. Encouragingly, problems of this type have recently become accessible to the computational modelling by clever combinations of the 'ab initio' Car-Parrinello Molecular Dynamics (CPMD) technique with the Path Integral Molecular Dynamics (PIMD) approach. Such an approach is considered in the STIPOMAT Programme in order to explore possibilities for a more accurate description of forces in such systems containing smart polymers.

Furthermore, on the mesoscale, it is still necessary to complement the already rather coarse Monte Carlo techniques, DPD and Lattice Boltzmann dynamics by still simpler methods suitable for faster computations on still longer length scales, such as the numerical self-consistent field approach and its extension to deal with dynamical properties. The STIPOMAT network provides a perfect framework for the various theoretical groups specialising in all these techniques to interact among themselves, share the techniques and develop them further, and make them fruitful for various specific systems and experimental applications, helping the synthetic chemists and experimental physicists to develop new types of stimuli-responsive polymeric systems and to understand their behaviour and properties.

Scientific activities in the STIPOMAT Programme

Workshops and conferences
The Steering Committee organises international workshops with around 40 participants which are held about once a year. The main contributors to the 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 Steering Committee. Contact between different teams both at the national and international level will be organised using electronic telecommunication including organisation of teleconferences. The role of the Internet and especially the Grid in communication, sharing the data and integrating of joint work in the framework of this Programme will increase with time.

Short-term fellowships
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 scope. Short-term fellowships 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 scientific visit grants
These cover the costs of short visits of senior researchers working in the area of the Programme, in order to carry out joint work primarily in one of the STIPOMAT participating laboratories.

Funding

- Fonds zur Förderung der wissenschaftlichen Forschung in Österreich (FWF)
  Austrian Science Research Fund, Austria
- Fonds National de la Recherche Scientifique (FNRS)
  National Fund for Scientific Research, Belgium
- Forskningsrådet for Natur og Univers (FNU)
  Natural Science Research Council, Denmark
- Eesti Teadusfond
  Estonian Science Foundation, Estonia
- Suomen Akatemia/Finlands Akademi
  Academy of Finland, Finland
- Centre National de la Recherche Scientifique (CNRS)
  National Centre for Scientific Research, France
- Deutsche Forschungsgemeinschaft (DFG)
  German Research Foundation, Germany
- Vetenskapsrådet (VR)
  Swedish Research Council, Sweden
- Schweizerischer Nationalfonds (SNF)
  Swiss National Science Foundation, Switzerland

STIPOMAT Steering Committee

Professor Jean-François Gohy (chair)
Unité de Chimie des Matériaux Inorganiques et Organiques (CMAT)
Département de Chimie
Université catholique de Louvain
Place L. Pasteur 1
1348 Louvain-la-Neuve
Belgium
Tel: +32 10 479269
Fax: +32 10 479269
Email: gohy@chim.ucl.ac.be

Dr. Alvo Aabloo
Institute of technology
University of Tartu
Vanemuise 21
51014 Tartu
Estonia
Tel: +37 2 7 375 534
Fax: +37 2 7 374 900
Email: alvo.aabloo@ut.ee

Professor Kurt Binder
Johannes Gutenberg – Universität
Condensed Matter Group
Institut für Physik
Staudingerweg 10
55099 Mainz
Germany
Tel: +49 6131 3923348
Fax: +49 6131 3925441
Email: Kurt.binder@uni-mainz.de

Professor Filip Du Prez
Ghent University
Department of Organic Chemistry
Polymer Chemistry Research Group
Krijgslaan 281 (S4-bis)
9000 Ghent
Belgium
Tel: +32 9 264 45 03
Fax: +32 9 264 49 72
Email: Filip.Duprez@ugent.be

Professor Ulf W. Gedde
Department of Polymer Technology
Royal Institute of Technology
100 44 Stockholm
Sweden
Tel: +46 8 790 76 40
Fax: +46 8 790 69 46
Email: gedde@polymer.kth.se

Professor Soeren Hvilsted
Danish Polymer Centre
Department of Chemical Engineering
Building 423
Technical University of Denmark
2800 Kgs. Lyngby
Denmark
Tel: +45 45 25 29 65
Fax: +45 45 88 21 61
Email: sh@kt.dtu.dk

Professor Alexei Khokhlov (Advisory Expert)
Physics Department
Moscow State University
Russia
Tel: +7 095 939-1013
Tel: +7 095 135-7910
Fax: +7 095 939-2988
Email: khokhlov@polly.phys.msu.ru

Professor Harm-Anton Klok
Ecole Polytechnique Fédérale de Lausanne (EPFL)
Institut des Matériaux
Laboratoire des Polymères
STI - IMX - LP
MXD 112 (Bâtiment MXD)
Station 12
1015 Lausanne
Switzerland
Tel: +41 21 693 4866
Tel: +41 21 693 4331 (secr.)
Fax: +41 21 693 5650
Email: harm-anton.klok@epfl.ch

Professor Françoise Lauprêtre
Laboratoire de Recherche sur les Polymères
Université Paris 12 Val de Marne and CNRS
2 à 8 rue Henri Dunant
94320 Thiais
France
Tel: +33 1 49 78 12 86
Fax: +33 1 49 78 12 08
Email:
Francoise.Laupretre@glvt-cnrs.fr

Professor Franz Stelzer
Institute of Chemistry and Technology of Organic Materials
Stremayrgasse 16
8010 Graz
Austria
Tel : +43 316 873 8450
Fax: +43 316 873 8951
Email: franz.stelzer@tugraz.at

Professor Heikki Tenhu
Laboratory of Polymer Chemistry
University of Helsinki
PB 55
00014 Helsinki
Finland
Tel: +358 9 191 50334
Fax: +358 9 191 50330
Email: heikki.tenhu@helsinki.fi

ESF Liaison

Dr. Patrick Bressler
Science

Ms. Chantal Durant
Administration

Physical and Engineering Sciences Unit (PESC)
European Science Foundation
1 quai Lezay-Marnésia
BP 90015
67080 Strasbourg cedex
France
Tel: +33 (0)3 88 76 71 27
Fax: +33 (0)3 88 37 05 32
Email: cdurant@esf.org

For the latest information on this Research Networking Programme consult the STIPOMAT websites:
www.chim.ucl.ac.be/stipomat
www.esf.org/stipomat

GRAFILEX - Print run: 1 500 - 02/07

EUROPEAN SCIENCE FOUNDATION
SETTING SCIENCE AGENDAS FOR EUROPE

1 quai Lezay-Marnésia I BP 90015
67080 Strasbourg cedex I France
Tel: +33 (0)3 88 76 71 00 I Fax: +33 (0)3 88 37 05 32
www.esf.org