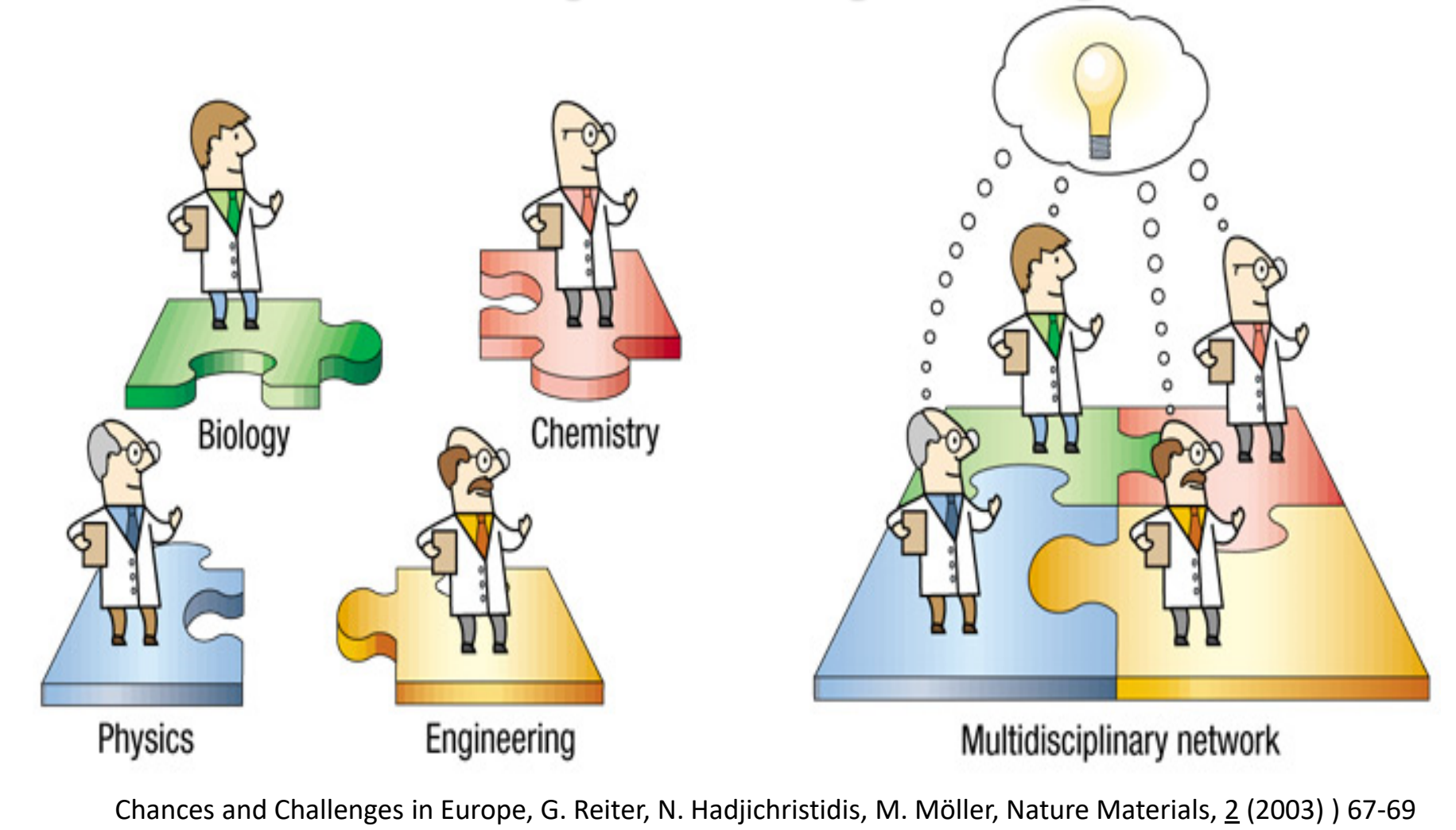


Interdisciplinary Projects:



Chances and Challenges in Europe, G. Reiter, N. Hadjichristidis, M. Möller, Nature Materials, 2 (2003) 67-69

Scientific orientation of the group

Experimental physics, especially in the field of "Soft Matter" provides an essential link between (Macromolecular) Chemistry, Biology and Applied Sciences. This is particularly true in the understanding and control of complex molecular systems and materials, which to some extent are inspired by processes found in nature.

The tasks of physics are mainly to identify the fundamental processes and to set parameters that describe them, to develop appropriate models based on predictions or requirements regarding their implementation in appropriate applications. Polymer physics, therefore, represents a fundamental pillar in terms of fundamental and conceptual issues in an interdisciplinary approach of innovative materials research. Research concentrates on questions dealing with properties of surfaces and interfaces, growth and structure formation processes, functional materials based on complex, nano-structured systems. Emphasis is on the study of molecular interactions, which control organization and structure formation.

The group follows a "bottom-up approach": molecular interactions and their control on a sub-nanometer scale determine the hierarchical organization of complex and functional (macro-) molecules over many length scales up to macroscopic lengths. These structures are made visible, the underlying ordering processes are identified and structure formation is varied and controlled by appropriate manipulation (external factors). Emphasis is intentionally placed on surface phenomena, because the corresponding (quasi-) two-dimensional systems allow for a set of experimental approaches and on the other hand, these phenomena play a central role in materials research.

Behavior and properties of polymers at interfaces and surfaces

In attempting to reduce the size of functional devices, the thickness of polymer films has reached values even smaller than the diameter of the unperturbed macromolecules. However, despite enormous efforts for more than a decade, our understanding of the origin of some puzzling properties of such thin films is still not satisfactory and several peculiar observations remain mysterious. For example, under certain conditions, such films show negative expansion coefficients or show undesirable rupture although they are expected to be stable. Some of these extraordinary effects can be related to residual stresses within the film, resulting from the preparation of these films from solution by fast evaporation of the solvent. Consequently, depending on thermal history and ageing time, such films show significant changes even in the glassy state, which we quantify by dewetting experiments and corresponding theoretical studies. Identifying the relevance of frozen-in polymer conformations gives us a handle for manipulating and controlling properties of nanometric thin polymer films. In this context, entropic energy contributions have to be explicitly emphasized as they represent a key difference between polymers and simple molecules. A basic understanding of the influence of conformational changes is expected to explain the behavior of polymers at interfaces.

Typical questions that are investigated in the group concern topics of:

- wetting and dewetting, adhesion and friction
- stability and morphological changes due to intermolecular interactions
- aging and relaxation behavior of polymers in restrictive spaces

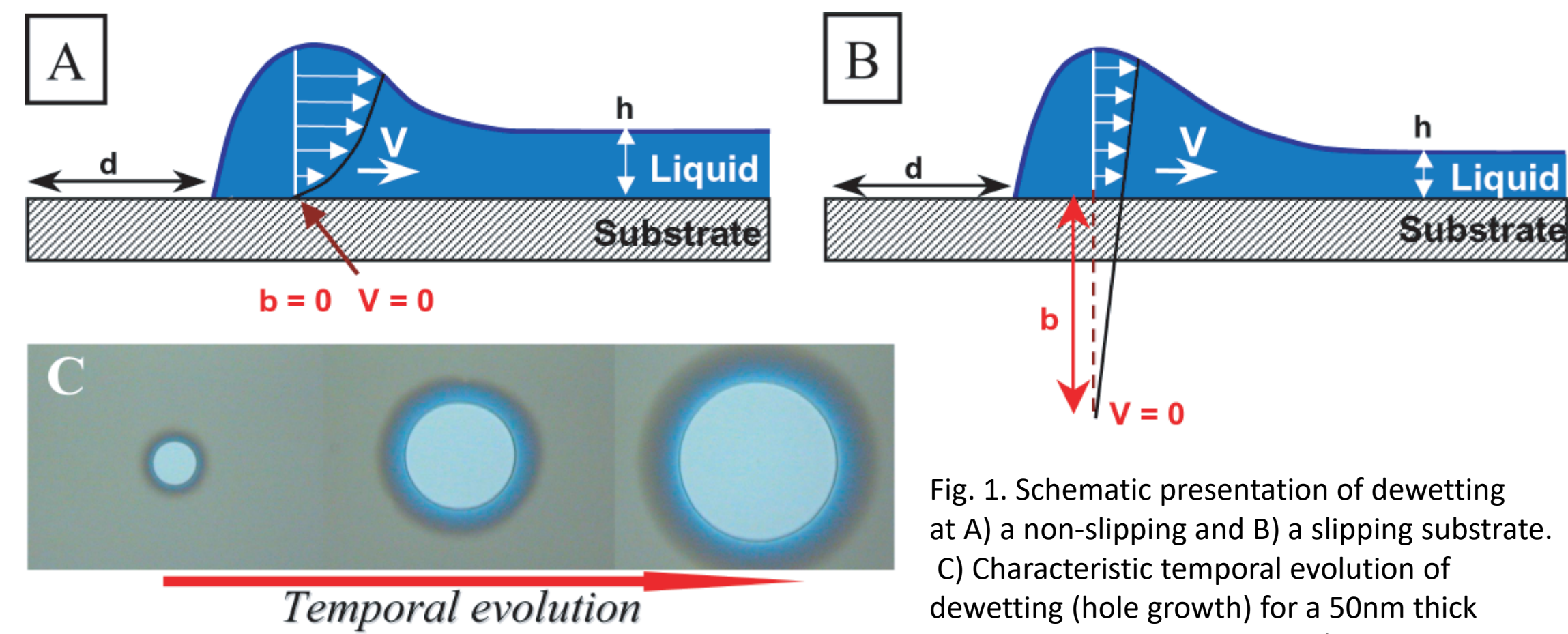


Fig. 1. Schematic presentation of dewetting at A) a non-slipping and B) a slipping substrate. C) Characteristic temporal evolution of dewetting (hole growth) for a 50nm thick polystyrene film (Mw = 52 kg/mol) at 120°C for 5, 30 and 60min, respectively. The size of each of the three images is 59 x 47 μm².

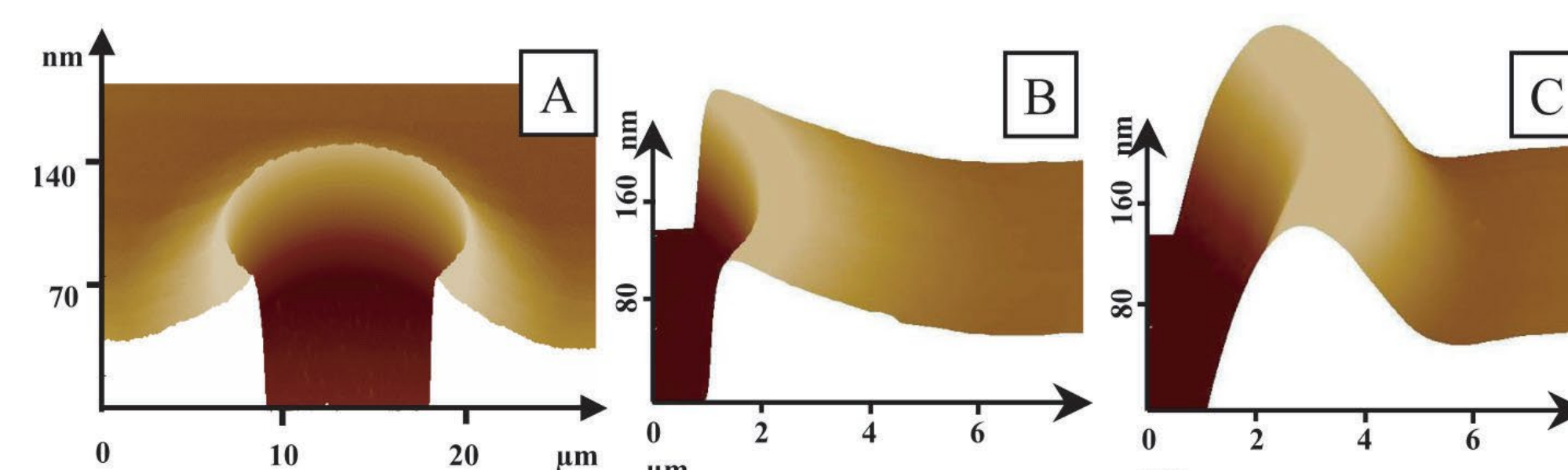


Fig. 2. 3D-view (measured by atomic force microscopy) of a typical hole obtained by dewetting a polystyrene film on a PDMS-coated substrate at temperatures close to the glass transition of PS. Typical 3D-cross-section of B) the asymmetric shape of the rim at early stages and comparatively low temperatures and C) the more symmetric shape at late stages or at high temperatures.

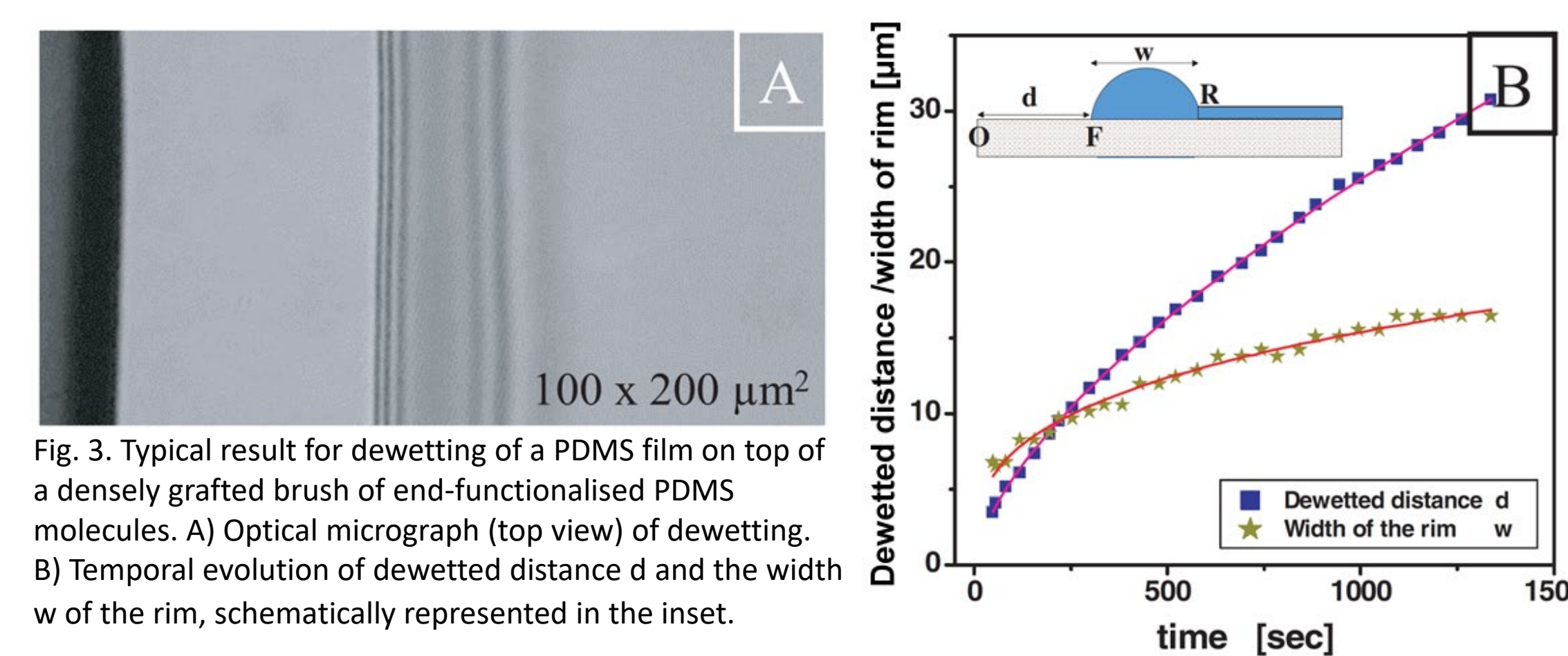


Fig. 3. Typical result for dewetting of a PDMS film on top of a densely grafted brush of end-functionalised PDMS molecules. A) Optical micrograph (top view) of dewetting. B) Temporal evolution of dewetted distance d and the width w of the rim, schematically represented in the inset.

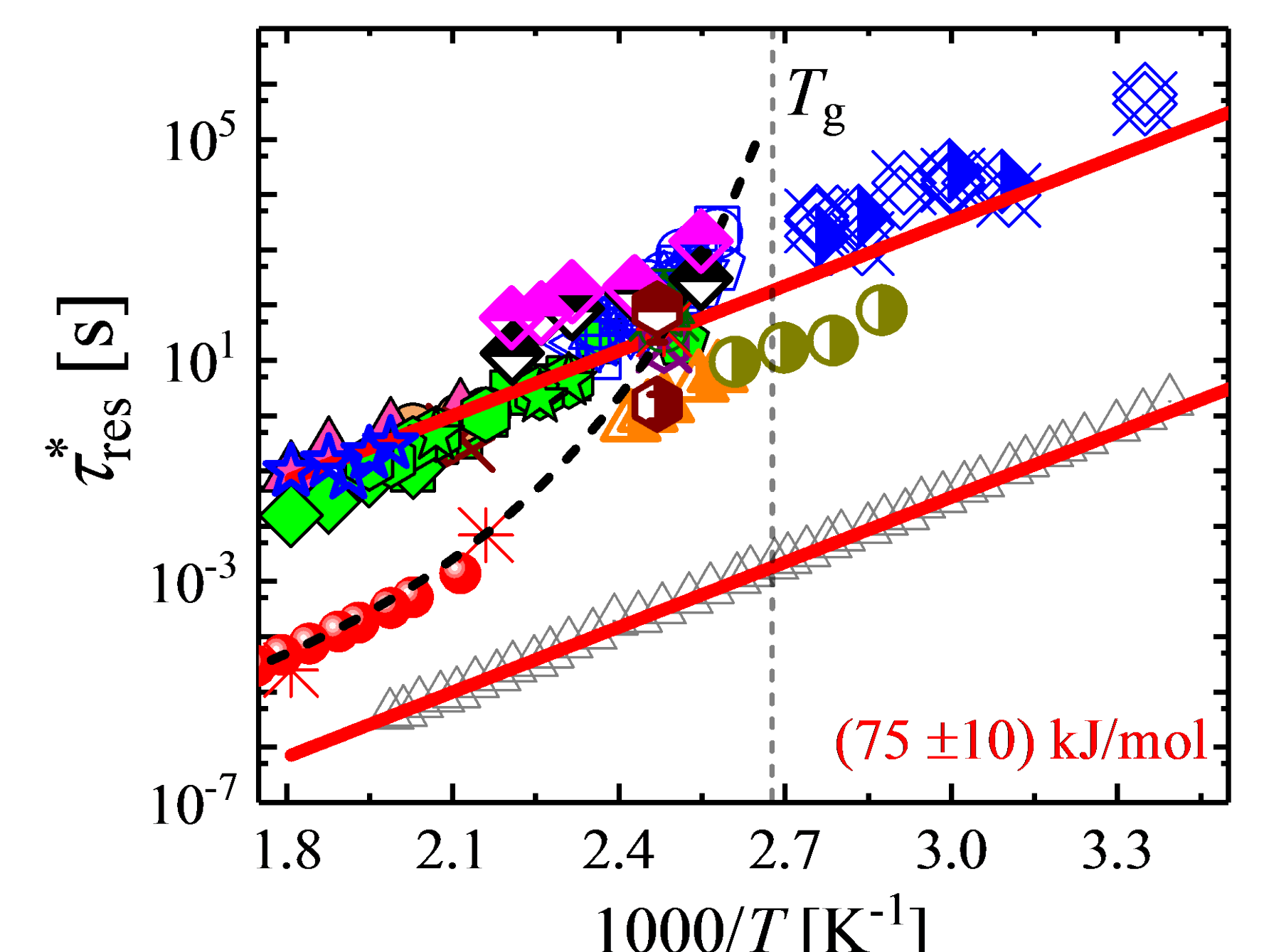


Fig. 4. Evolution of the scaled residual stress relaxation time τ_{res}^* with dewetting temperature (T) from various dewetting and complementary experiments.

Growth processes in complex systems

Structures resulting from growth processes like crystallisation or gradient-driven assembly are formed at a finite rate, and thus under non-equilibrium conditions. Thus, they typically depend on kinetic parameters governing nucleation and growth, may result from rapid changes of temperature, fast solvent evaporation, or the kinetics of adsorption and phase separation. Consequently, these materials are normally not perfectly ordered and often relax in time which leads to morphological reorganisation, ageing or morphogenesis. An advantage of such growth processes is the possibility to generate a multitude of different structures and functional patterns from one single molecular system, simply by varying the conditions of the ordering processes. In this context, macromolecules represent versatile systems for complex growth processes where a subtle balance between various physico-chemical processes and the sensitivity to even the slightest variations of the growth conditions determine the resulting morphologies and functional patterns. For predicting and controlling the resulting structure and function it is not sufficient to design, tailor and put together the right chemical units forming the macromolecules. A comprehensive understanding of growth and ordering processes is necessary in order to control and tune the assembly of these molecules over multiple length-scales up to functional macroscopic objects.

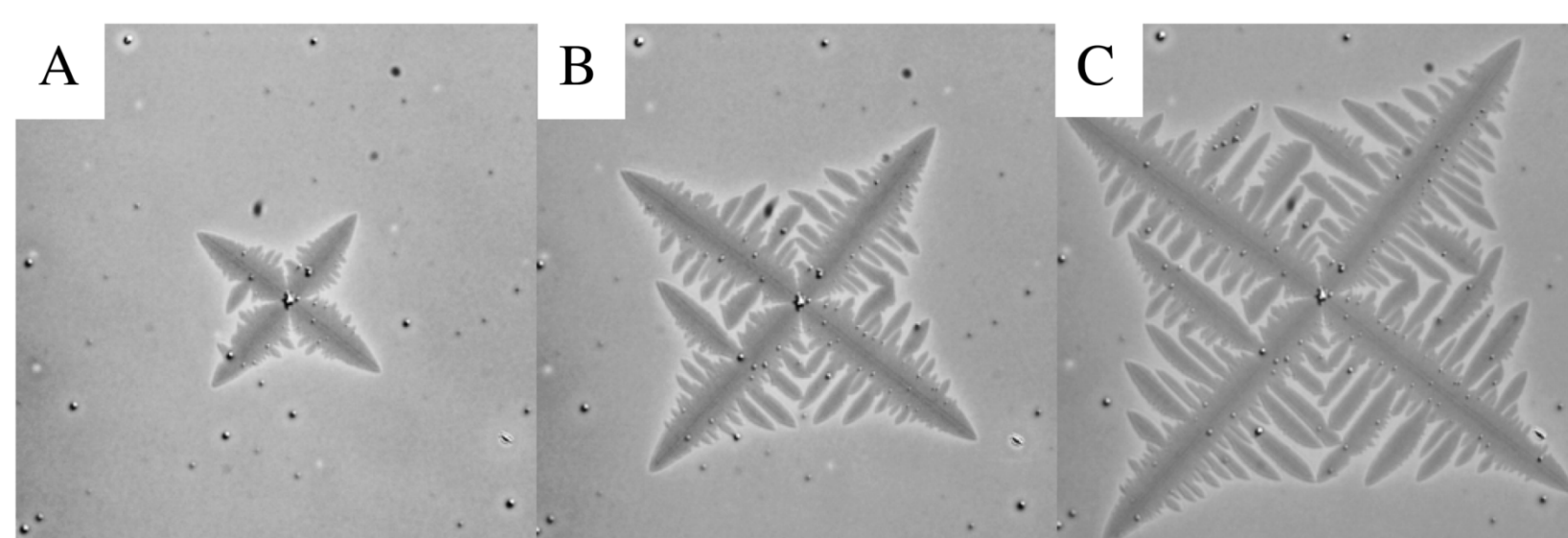


Fig. 5. Optical micrographs of the growth of a polymer crystal in a ca. 35nm thick film. The images were taken after A) t_0 , B) t_0+30 min, and C) t_0+60 min. The average growth rate of the diagonals from center to tip is about 0.9 μm/min. The size of the images is 115 x 115 μm².

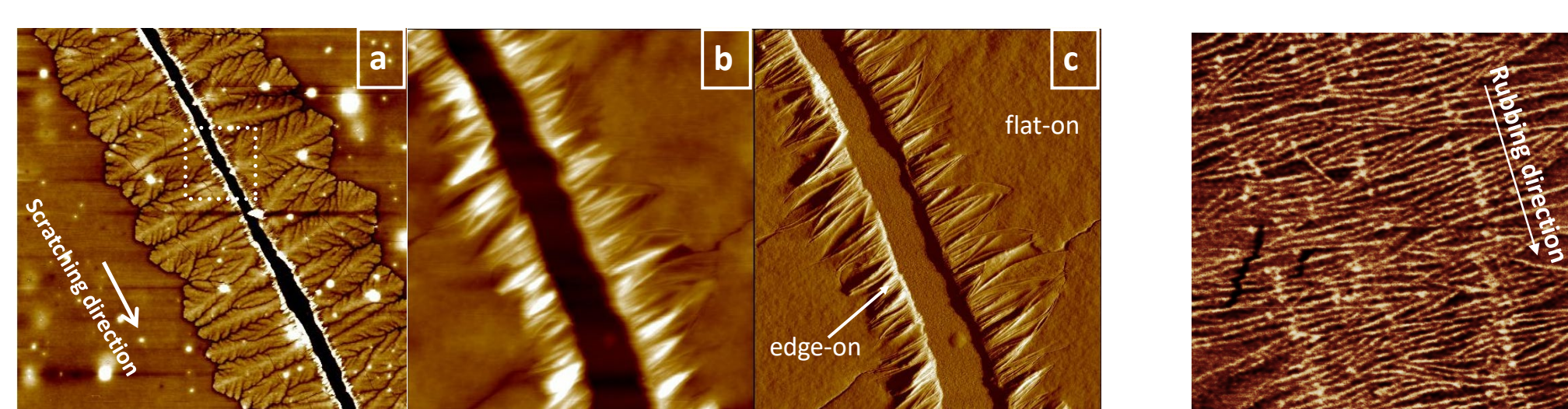


Fig. 6. AFM images showing the orientation of isotactic polystyrene crystal lamellae obtained after isothermal crystallization of a scratched thin film. a) Topographic image (size: 45x45 μm²; height range: 30 nm). The branched features represent flat-on lamellar crystals. b, c) Topographic and phase mode image of the region indicated by the dotted box in a) (size: 5x5 μm²; height range: 60 nm) representing edge-on lamellae, continued by flat-on lamellae, oriented perpendicular to the scratching direction.

Isothermal crystallization of the rubbed thin film: phase image (size: 1 x 1 μm²)

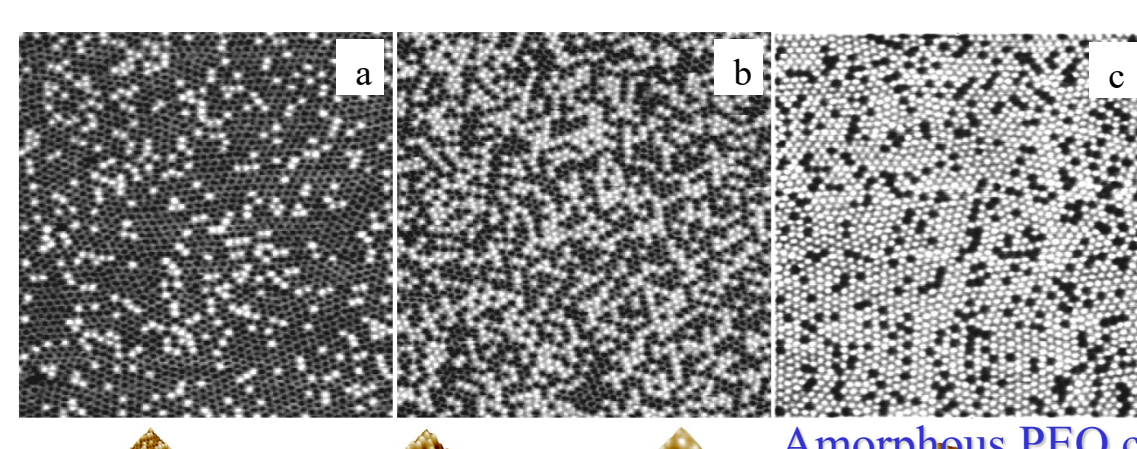


Fig. 7. AFM phase images (1 x 1 μm²) representing the variation in the number and the distribution of crystalline cells in a thin PBz-PEO (21.1–4.3) film after crystallization at -23°C for (a) 5 min, (b) 15 min, and (c) 120 min, respectively. Images (d)–(g) are enhanced 3D representations of (b) at different magnifications: (d) 1 x 1 μm², (e) 500 x 500 nm², (f) 250 x 250 nm², and (g) 100 x 100 nm².

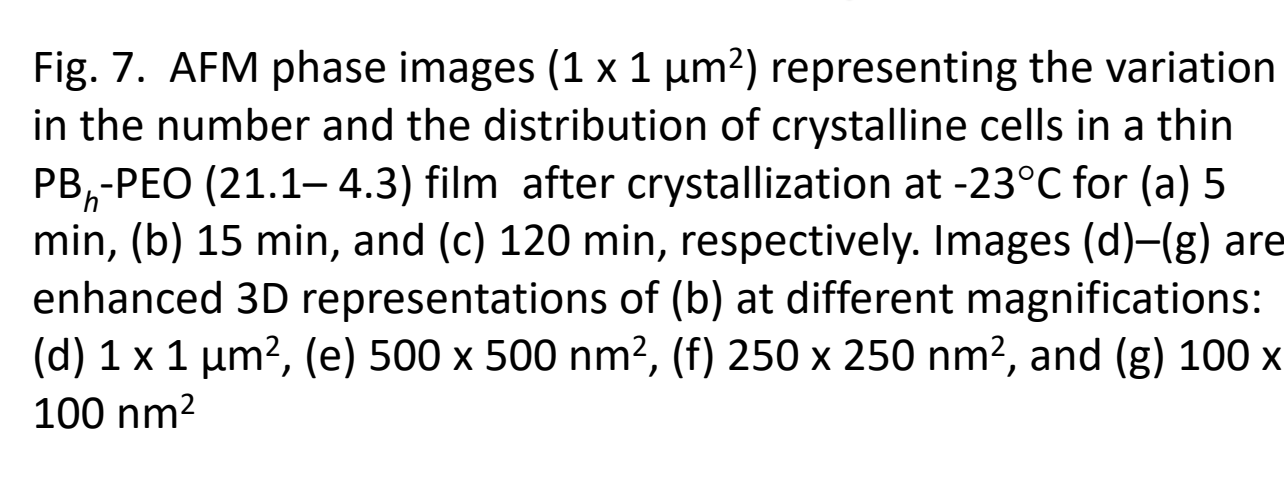


Fig. 8. Controlled melting of crystalline PEO cells with an AFM tip.

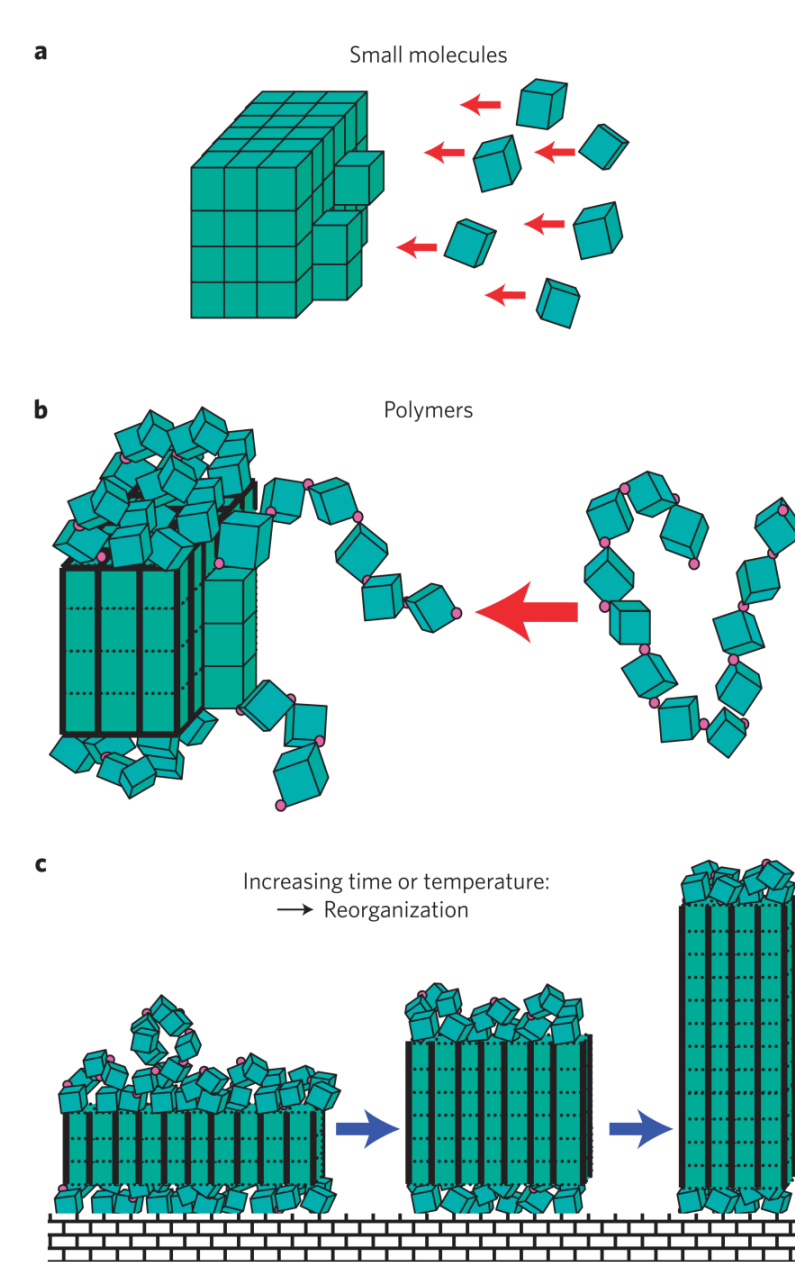


Fig. 9. Schematic presentation of essential steps in polymer crystallization enabling cloning.

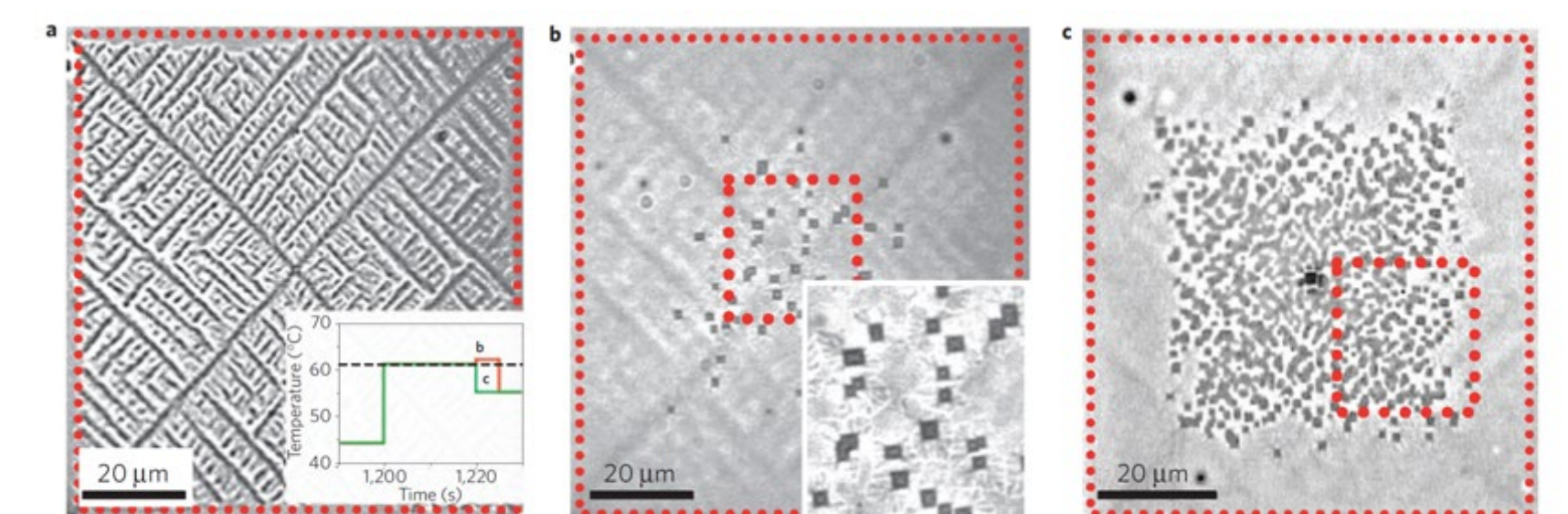
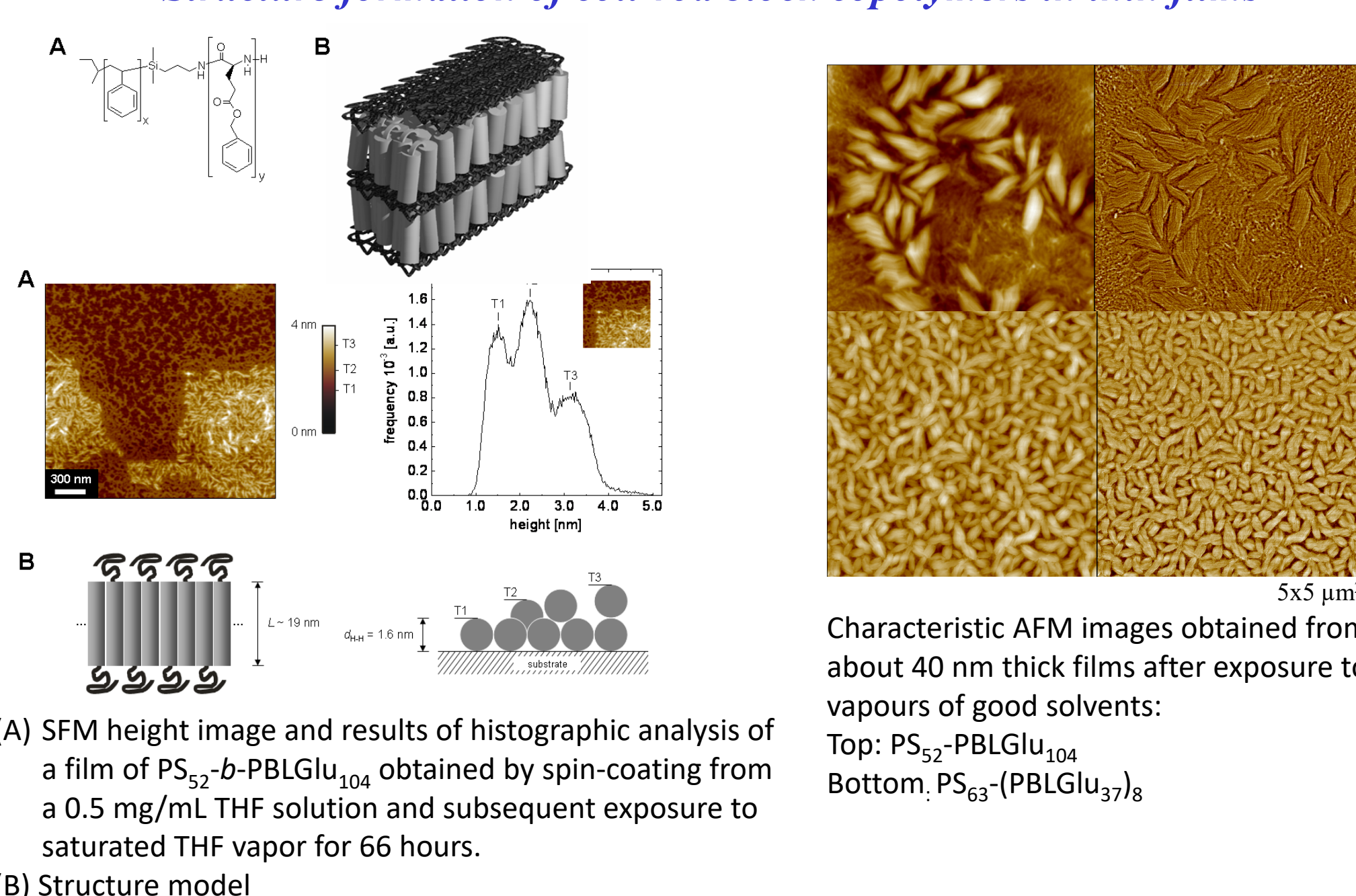


Fig. 10. Transforming a large compact dendritic single crystal into a plethora of uniquely oriented small crystals. a, The starting crystal of P2VP-b-PEO, outlined by a dotted red square, after 22 min at 45°C. The inset shows the temperature protocol used for the samples shown in b, c. The dashed line indicates the nominal melting temperature. b, After an extra 20 s at 62°C plus 5 s at 63°C, and 4 min at 56°C followed by a quench to room temperature. The inset shows a magnification of the central area indicated by the dotted square. c, Another crystal analogous to a was annealed for 20 s at 62°C before it was recrystallized for 3 min at 56°C and then quenched to room temperature. d, e, AFM images of the selected regions of sample c. The red arrows in e indicate the orientation of the seeding crystal. f, Probability of orientation of the cloned crystals with respect to the seeding crystal.

Molecular self-assembly and formation of functional structures on surfaces

Nature has followed a large number of pathways in organising molecules for the creation of functional materials and systems. Extraordinary properties and functionalities are introduced by a hierarchical organisation at different length-scales. Molecular processes of spontaneous self-organization, especially at interfaces, allow the creation of functional and controllable structures. In this context, long-range ordered supra-molecular structures with sub-molecular precision have to be mentioned. The understanding of organizational processes and their precise control over several length scales of time is essential in order to obtain operational building blocks of artificial functional systems.

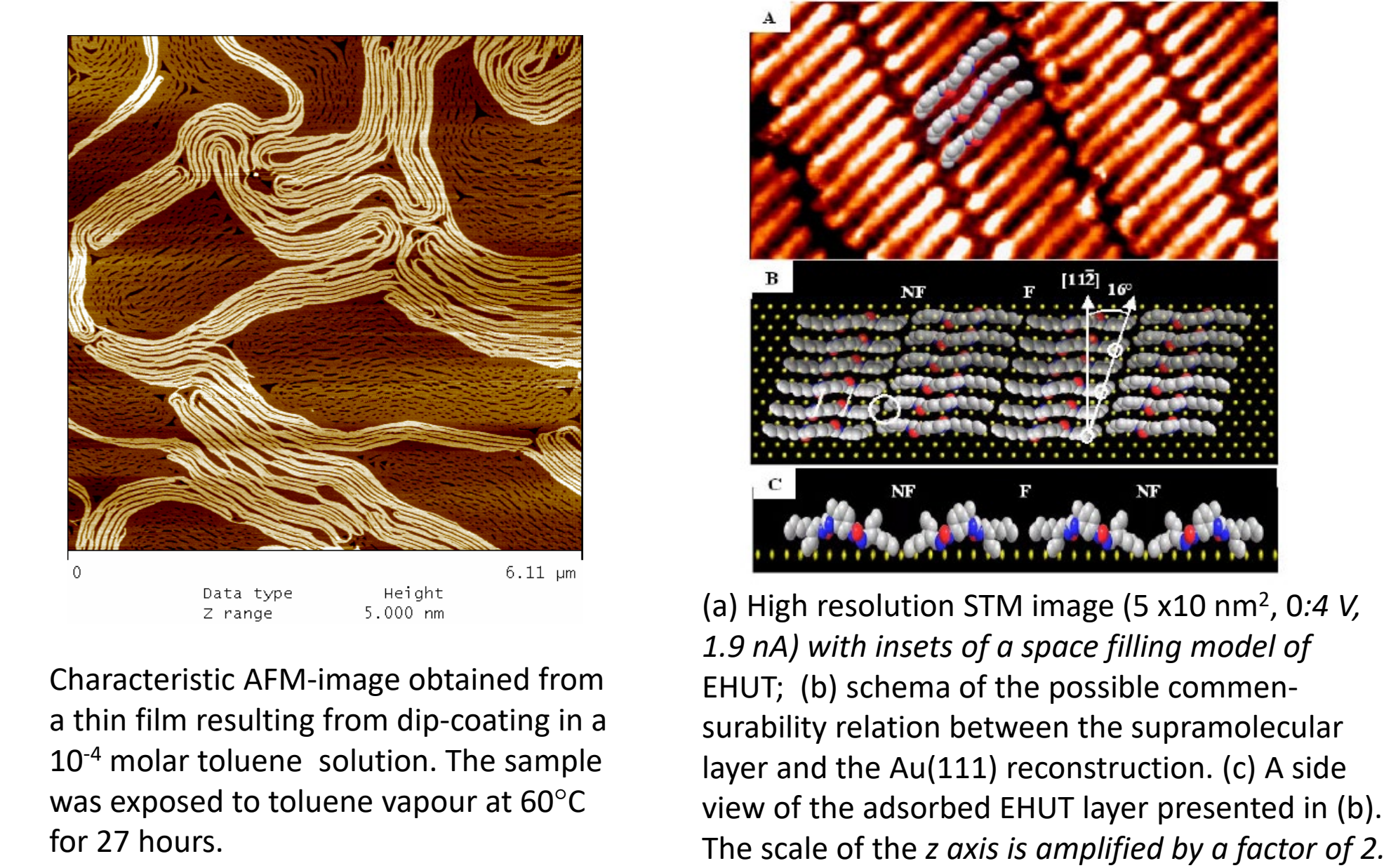
Structure formation of coil-rod block copolymers in thin films



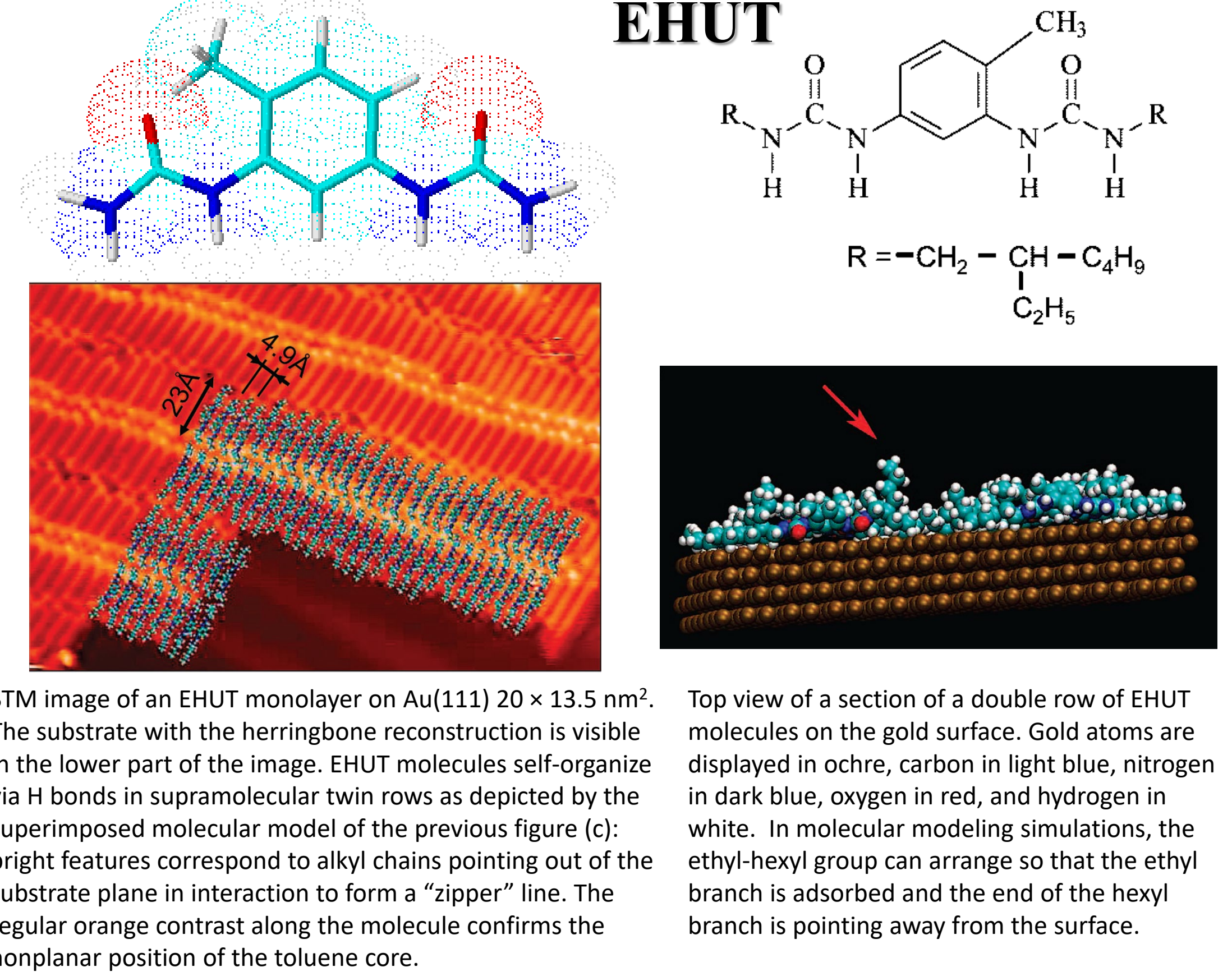
The structure formation of a polystyrene-block-poly(L-benzyl-L-glutamate) (PS-PBLGlu) with an amorphous and a crystallizable, helical segment has been investigated in thin films and compared to the situation in the bulk. Thin films were prepared by spin-coating from dilute tetrahydrofuran (THF) solution and subsequently annealed in saturated THF vapor to achieve a controlled crystallization of PBLGlu. Analysis of the films with scanning force microscopy (SFM) reveals a variety of structures with ordering on several length-scales, ranging from a few nanometers to microns.

Evolution of Multilevel Order in Supramolecular Assemblies

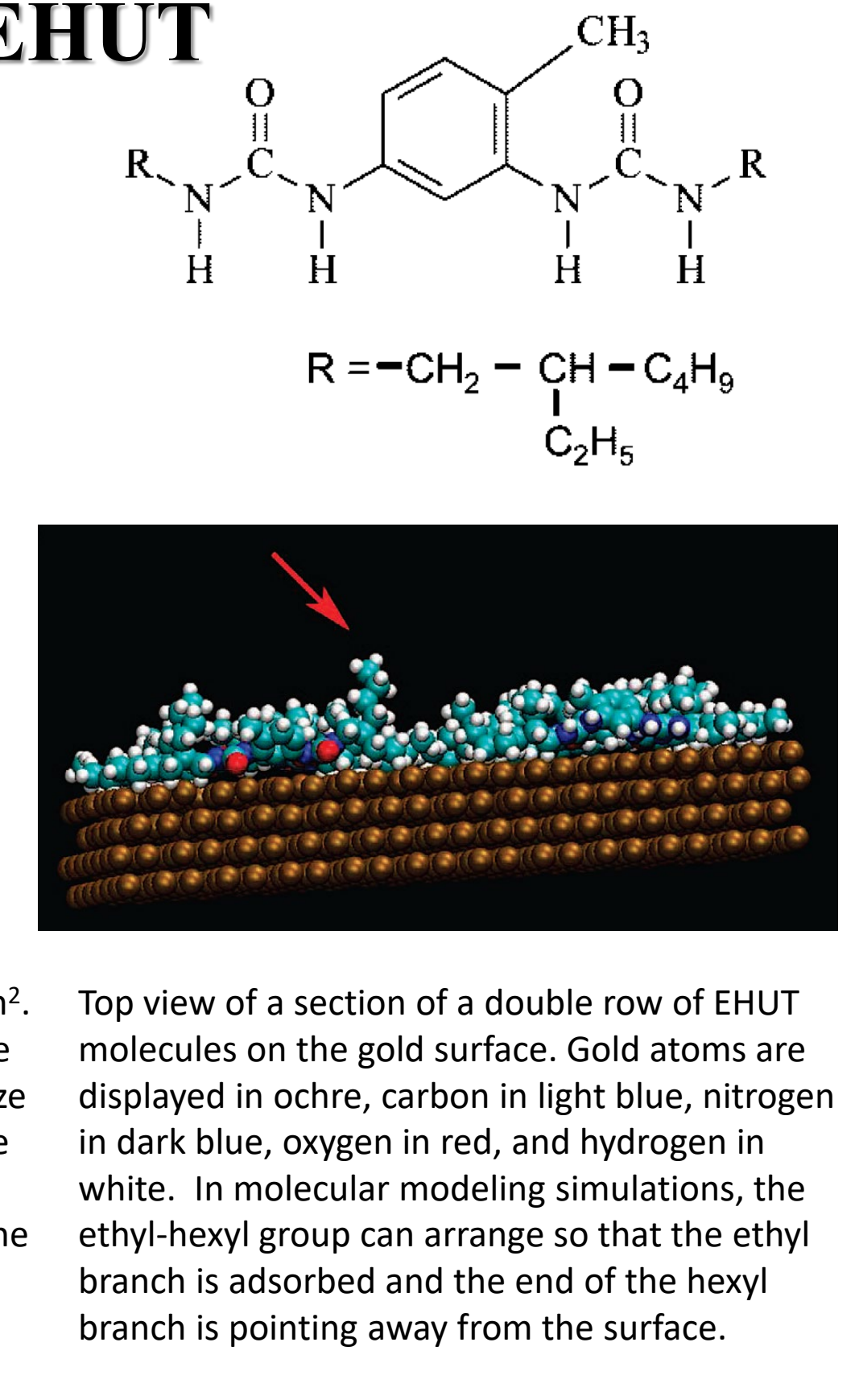
The process of self-assembly at multiple length scales of bis-urea substituted toluene on a Au(111) surface was studied by low temperature scanning tunneling microscopy. Pattern formation is controlled by specific hydrogen bonds between these molecules but also by significantly weaker lateral coupling between the resulting supramolecular polymers and a quasiepitaxial interlocking with the substrate. The ordered assemblies exhibit a tunnel transparency. Our experiments indicate the necessity of multiple interactions of different strengths for obtaining ordered structures with hierarchical levels of organization.



(a) High resolution STM image (5 x 10 nm², 0.4 V, 1.9 nA) with insets of a space filling model of EHUT; (b) schema of the possible commensurability relation between the supramolecular layer and the Au(111) reconstruction. (c) A side view of the adsorbed EHUT layer presented in (b). The scale of the z axis is amplified by a factor of 2.



STM image of an EHUT monolayer on Au(111) 20 x 13.5 nm². The substrate with the herringbone reconstruction is visible in the lower part of the image. EHUT molecules self-organize via H bonds in supramolecular twin rows as depicted by the superimposed molecular model of the previous figure (c): the bright features correspond to alkyl chains pointing out of the substrate plane in interaction to form a "zipper" line. The regular orange contrast along the molecule confirms the nonplanar position of the toluene core.



Top view of a section of a double row of EHUT molecules on the gold surface. Gold atoms are displayed in ochre, carbon in light blue, nitrogen in dark blue, oxygen in red, and hydrogen in white. In molecular modeling simulations, the ethyl-hexyl group can arrange so that the ethyl branch is adsorbed and the end of the hexyl branch is pointing away from the surface.