Functional polymers: scanning force microscopy insights†

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Scanning force microscopy (SFM) and related techniques make it possible to visualize polymer systems with a molecular resolution. Beyond imaging, they also enable the unveiling of a variety of (dynamic) physico-chemical properties of both isolated polymer chains and their supramolecular architectures, including structural, mechanical and electronic properties. This article reviews recent progress in the use of SFM on polymers, with a particular emphasis on the mechanical properties of copolymers and single polymer chains, as well as on the bottom-up fabrication of supramolecular polymeric (helical) nanostructures in particular based upon π-conjugated macromolecules as building blocks for nanoelectronics. Through a detailed understanding of the polymer behavior, we propose solutions for the generation of organic functional (nano)systems.

SFM in polymer science

The physico-chemical properties of molecules and macro-molecules strongly depend on the "molecular sociology", namely on the way the molecules interact among them and with external bodies, such as a solid substrate surface. The generation of functional materials "from the bottom-up" requires the tuning of the hierarchical self-organization, and consequently of a variety of properties, across a wide range of length scales, from the molecular to the macroscopic scale.[1–4]

The technique

The invention of scanning probe microscopies (SPM)[5] has boosted the investigations of a large variety of physico-chemical properties of very small objects, including isolated molecules and polymers, as well as their macroscopic architectures. As a result, those techniques now constitute a fundamental tool in materials science.[6,7] In particular atomic force microscopy (AFM), also known as scanning force microscopy (SFM),[8] is an extremely versatile technique which makes it possible to study, in a mildly non-invasive manner, both electrically-insulating and -conductive nanostructures with a resolution below 3 nm.[9,10] The development of SFM rendered it possible to study polymers and bio-molecules, which typically possess poor electrical properties.[11,12] The prime physical property employed to map the surface by SFM is the interaction force between a sharp solid tip and the sample surface. The probes employed, typically made of Si or Si_3N_4, are microfabricated, conically-shaped tips, having a radius of curvature below 10 nm, mounted at the edge of a flexible cantilever. The interaction between tip and surface, which can be approximated to be of van der Waals type, induces a bending of the cantilever, which is recorded using the beam-bounced detection mode, and translated to give a real physical quantity, e.g. the topography of the surface. The cartoon in Fig. 1 highlights the operating principle of SFM.

Dynamic modes of SFM (i.e., using an oscillating probe) have been first conceived to minimize the contact between the tip apex and the surface, while keeping the ability of measuring weak variations of the force. Thus, images can be recorded with only a very brief intermittent contact over a cycle of oscillation or even with no contact at all (the 'contact' being defined as a situation where very short-range repulsive forces dominate the tip–sample interaction). As a result, if not totally removed, the shear forces are significantly reduced. The development of dynamic modes can be seen as a breakthrough in scanning force microscopy as their ability to probe minute forces has opened avenues in imaging soft materials reproducibly and routinely, even reaching atomic resolution in ultra high vacuum conditions. Two modes of operation can be considered for measuring changes of the oscillating behavior when the tip interacts with a surface: (i) the amplitude modulation (AM) typically called "tapping" mode, in which the tip–cantilever system is excited at a fixed drive frequency and a given amplitude[13] and (ii) the frequency modulation (FM) technique; it is often called "non contact resonant" mode.[14] For the FM mode, the basic idea is to use a negative resonant frequency shift at constant oscillation amplitude as the error signal to control the distance between the tip and the surface. In doing so, the interaction between the tip and the surface remains attractive so that the tip never 'touches' the surface.

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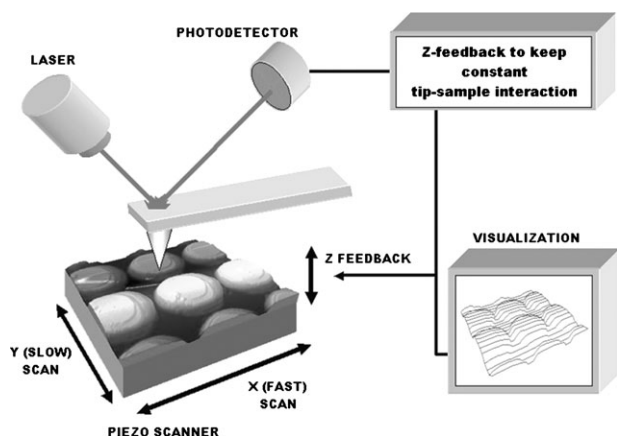† The HTML version of this article has been enhanced with additional colour images.

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The SFM measurements can be performed at various interfaces including solid–gas, solid–vacuum and solid–liquid; thus they enable studies not only of static properties, but also dynamic processes in solution, such as (macro)molecular motions or chemical reactions occurring at surfaces, *etc*. Since the end of the 1980s, SFM techniques allowed the generation of very fascinating images, providing a direct view into the nanoworld. Chemists, physicists and engineers quickly realized the disruptive potential of these techniques and started to bestow more and more information on nanoscale objects, expanding their research beyond imaging,[6] thereby exploring the physico-chemical properties of matter in a quantitative manner and finally employing the obtained information to optimize the properties of functional (nano)materials. Moreover, the use of the SFM tip to manipulate objects, for instance functionalized macromolecules, in combination with the possibility of using external stimuli to trigger molecular reactions, *e.g.* light, makes it possible to nano-construct new polymeric architectures by photochemically covalently linking two isolated macromolecular strands.[15] SFM therefore offers new approaches to explore many (dynamic) properties of molecules and molecule-based architectures across a wide range of length scales, and therefore appears to be an ideal tool for polymer science.

In the present review we highlight a series of fascinating results of SFM studies on polymers, with a particular emphasis on the mechanical response and properties of polymer and polymer-based architectures, as well as on the formation of supramolecular functional assemblies from π-conjugated polymers, some of them showing the unique propensity to form helical nanostructures.

Basic properties of macromolecules at surfaces

The SFM studies of polymers at surfaces rely on the adsorption on solid substrates. In a broader context, the processability of giant (macro)molecules into ultra-pure and highly ordered structures at surfaces is of fundamental importance for studying chemical, physical and biological phenomena, as well as their exploitation as active units in the fabrication of hybrid devices.[16] Macromolecules are processed at surfaces usually from solution, thus the choice of the substrate and solvent is crucial as the properties of the polymer in solutions, including their conformation, strongly depend on the interplay between solvent–macromolecule and macromolecule–macromolecule interactions. Different solution processing methodologies can be employed, such as spin-coating, drop casting and dipping (also under controlled atmosphere). While the former is a quite rapid process as it takes place in a few seconds, the latter is much slower and can last up to a few days. In all such processes, the self-assembly at surfaces is typically a kinetically-driven phenomena.[17] Nevertheless, the progress towards thermodynamic equilibrium can be fostered making use of post treatments such as thermal annealing. It was indeed recently shown[18] by SFM that the self-organization at surfaces of polysiloxane–phthalocyanine (PSPc) chains with a length of a few tens of nanometers into ordered rod-like architectures having a length up to 1 μm and a molecular cross-section can be improved upon thermal annealing (Fig. 2). This elongation of the rod-like architectures upon heating is probably due to the tendency of the rod-like polymers to pack in a head-to-tail motif, facilitated possibly by hydrogen bonding interactions between the Si(OH) end-groups. These nanocylinders, possessing a high apparent stiffness, may be good prototypes of molecular nanowires for future molecular scale electronics.
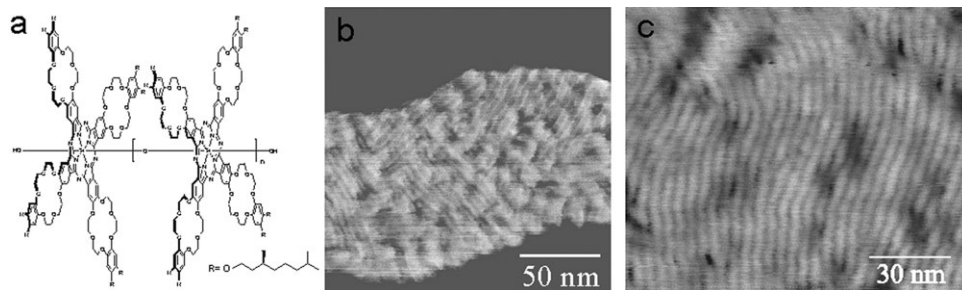
The growth of macromolecules into well-defined and oriented nano and microscopic motifs can be driven by the use of pre-patterned surfaces. Jonas and co-workers have fabricated surfaces made of aligned hydrophilic and hydrophobic tracks by a lithographic method involving self-assembled monolayers (SAMs). These textured surfaces have been used to orient the adsorption of globular proteins onto 20 nm-wide aligned domains.[19] Local oxidation of silicon surfaces into silicon oxide domains as induced by an SFM tip is another powerful nanolithography method to make pre-patterned substrates: Garcia, Biscarini and collaborators have successfully grown conjugated macromolecules into crystalline architectures aligned along the silicon oxide stripes on a silicon substrate, in the purpose of making defined 'wires' for organic electronics applications.[20]

Immobilization and diffusion

The visualization of a macromolecule by SFM requires its immobilization at the surface, to an extent that it does not move due to diffusional or other types of motions during measurements, at least with a rate faster than that of the tip scanning the surface. Moreover, the interaction between the molecule and the surface has to be stronger than the interaction forces between the molecule and the SFM tip during scanning, to avoid measurements being performed in an invasive regime. The use of non-contact or intermittent (e.g., tapping) mode,[13] when compared to contact-mode SFM, made it possible to notably decrease the magnitude of the tip–sample interactions, granting an almost non-invasive visualization of soft materials, such as polymer chains and biointerfaces.[21,22]

The subtle balance between intermolecular and interfacial interactions opens the door to real-time studies of the "diffusion" of polymer chains on surfaces. Recently Kumaki and co-workers showed that single high molecular weight poly(methyl methacrylate) chains adsorbed on mica in a humid environment diffuse according to a 'reptational' motion, i.e., along the chain axis (for comparison, as a caterpillar), see Fig. 3. Lowering the relative humidity (i.e., the thickness of the water layer on mica), the diffusion coefficient of the chains decreases. It is worth noting that the risk that the SFM tip could induce these 'reptational' movements is under debate, but arguments quite convincingly rule out this possibility.[23]

In contrast, Sheiko and collaborators[24] studied the spreading of a melt droplet of brush-like molecules on HOPG and observed a random-walk transport due to the plug flow of polymer chains on the substrate, with minor contribution from the diffusion of brush molecules (the spreading proceeds faster than the thermal diffusion). They demonstrated that the diffusion of brush molecules is not spontaneous but induced by the sliding of the dense monolayer over the heterogeneous substrate. It is important to point out that the latter two studies were performed on very different molecular systems, processing and substrates. It is remarkable how the variation of just a parameter (the relative humidity), tuned by the presence of solvent vapours, can significantly alter the conformation of single macromolecules; depending on that parameter, poly(isocyanodipeptide) chains adopt different conformations, which can be unravelled by their drastic thickness changes measured by SFM imaging.[25]

Molecular weight distribution estimation

One important property of a polymer compound is its molecular weight distribution. This characteristic is usually estimated with indirect methods including size exclusion chromatography (SEC), light scattering, viscometric or osmometric measurements or end-group analysis.[26] The absolute values obtained with these methods must often be taken with
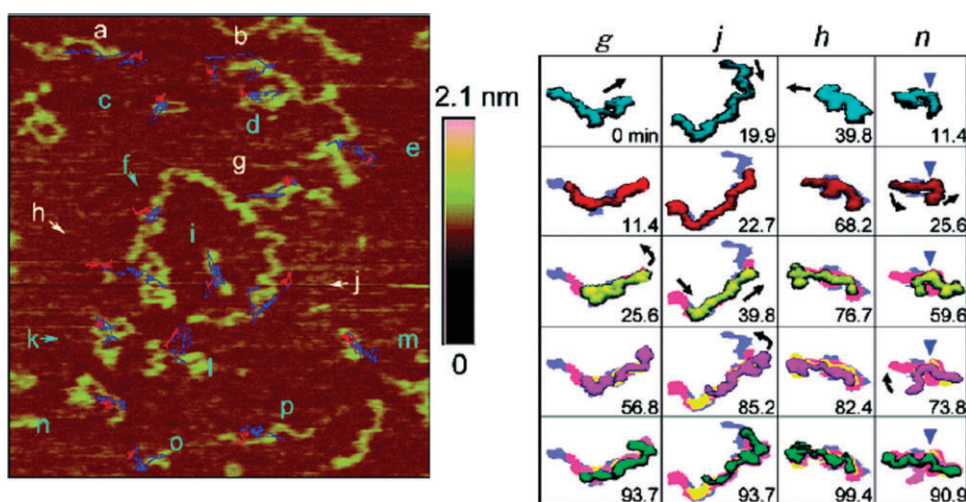

Fig. 3 Movements of isotactic poly(methyl methacrylate) chains adsorbed on mica under high humidity. Left: SFM image of isotactic PMMA chains on mica deposited by LB technique (time: 0 min; scale: 484×533 nm^2; scan direction. Each chain is indicated by 'a' to 'p' (freely moving chains: white; anchored chains: light blue). The trajectories of the center-of-mass of the chains are shown by blue lines from 0–82.5 min in 71% relative humidity (RH) and by red lines from 82.5–136.5 min in 54% RH. Right: Time lapse of the chain shapes for chains g, j, h, and n. The chain images are superimposed by changing the color from blue, orange, yellow, pink, and green with time. Reprinted with permission from J. Kumaki, T. Kawauchi and E. Yashima, *Macromolecules*, 2006, **39**, 1209. Copyright 2006 American Chemical Society.[23]

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caution, in particular due to problems related to the calibration of the set-ups (*e.g.*, related to the hydrodynamic volume of the investigated macromolecules for SEC studies) or because they are based on assumptions and models which might jeopardize the correct analysis. Moreover the tendency of molecules to aggregate in solution or when applied to the surface can render these measurements quite delicate. SFM imaging of single macromolecules provides a direct and quantitative estimation of the polymer contour length, thus of the molecular weight distribution of polymers.[27,28] This estimation requires that the molecules adopt a stretched conformation at surfaces. Given the length and the mass of a repeat unit, from the estimated contour length of a polymer chain, one can calculate its degree of polymerization and its molecular weight, respectively. Statistical analysis of a relevant set of macromolecules then provides the molecular weight distribution. In the case where the macromolecule does not adopt a stretched conformation when adsorbed at surfaces, such a conformation type can be triggered using a templating self-assembled monolayer physisorbed at surfaces, *e.g.* a 2D crystal of derivatized alkanes adsorbed on graphite.[29,30]

Local thermal analysis of (confined) thin films

Local thermal analysis allows one to measure the glass transition temperature (T_g) or the melting temperature as well as thermal conductivity/diffusivity of thin polymer films. A thermal probe mounted on a SFM is brought into contact with the sample and a step-and-hold temperature profile is applied.[31] The power at each temperature is measured, and a break in the temperature derivative of the power can be assigned to the transition. It is observed that the probe position changes as a function of the temperature and time. The question arises then as to whether the transition in the probe power is due to calorimetric effects or to the rheological behaviour. It appears that the contribution to the signal due to calorimetric effects (changes in conductivity, heat capacity, specific heat) can be separated from the contribution due to rheological effects (changes in viscosity and other viscoelastic parameters) and it is found that the T_g transition signal is entirely due to rheological effects. Sills and Overney applied the technique of low amplitude modulated SFM to study the temperature and time dependent response of bilayers of poly(methyl methacrylate) (PMMA) and poly(styrene) (PS) deposited on silicon substrates.[32] Glass transitions for both polymers are observed for thin (on the order of 100 nm) outer layers. By varying the layer thickness they were able to probe the sensitive volume of the measurement by recording the strength of the sublayer glass transition signal. With this technique, it is also possible to determine the relative weight of elastic and viscous forces on the SFM tip. Lateral Force Microscopy (LFM) can also be used to determine T_g of polymeric thin films, as the friction between the tip and polymer surface changes significantly when the glass transition takes place.[33,34]

SFM adhesion measurements can be employed as a direct probe to fully characterize the surface dynamics of model samples. Force–distance curves are recorded on thin films at different temperatures and the pull-off force at which detachment between the SFM tip and the sample occurs is measured

as adhesion.[35] Along the same line, Takahara and coworkers[36] developed scanning viscoelastic microscopy (SVM)[37] to study the surface modulus of polymer thin films. By the detection of an amplitude change in the response force signal as well as the phase lag between the stimulus displacement and the response force signals, surface viscoelastic properties can be extracted. They found that for monodisperse poly(styrene) thin films, the surface glass transition temperature is much lower than in the corresponding bulk material. These results unequivocally show that surface mobility in the thin film is much enhanced in comparison with the bulk. This shift of the glass transition temperature of polymers in confined geometries is attributed to the inhomogeneous density profile of the liquid.

Microscopic mechanical properties

One of the most important properties of polymer systems, in view of their application for the generation of functional materials, is their mechanical properties. Attempts to determine the elastic modulus and yield strength of polymer thin films by SFM have been reported.[38] Despite the success of SFM for microstructural characterization, important questions remain about the physical origin of the image contrast. The height images are generally considered to display topographic information, but it must be kept in mind that the local mechanical properties of the sample (*i.e.*, the possibility that the tip slightly penetrates the surface) may also contribute to the contrast in the height image. The discrimination between the mechanical and topographic responses in SFM images of viscoelastic materials (such as polymers) has become a critical issue. This latter issue has been recently addressed by characterizing designed model polymer systems containing two (or more) chemically-distinct components, such polymer blends or block copolymers.[39,40] Among the various block copolymer architectures described in the literature, the most commonly studied system consists in linear diblock or triblock copolymers combining thermoplastic and elastomer sequences. These materials, known as "thermoplastic elastomers", exhibit synergetic properties that fill the gap between pure rigid materials and soft elastomers and are therefore valuable alternatives to polymer blends. Because of the constraint imposed by the covalent bonding between the blocks and the typical molecular weight values of the blocks (between 5000 and 100 000), phase separation in block copolymers occurs at a length scale that is much smaller than for polymer blends. Along the same line, the very well-defined periodicity of the phase-separated domains makes these materials very interesting model systems for SFM measurements, in particular for quantitative investigations. The height image is obtained recording the vertical displacements of the piezo actuator necessary to maintain the oscillator amplitude at a pre-set value. The phase images correspond to the recording of the phase lag existing between the signal sent to the piezo (to force the tip to oscillate at a given fixed frequency) and the signal measured by the photodiodes (corresponding to the oscillations of the cantilever). This image gives information on the dissipated energy during the tip–sample interaction, and thus on the sample's local mechanical properties. When recording approach–retract curves, the sample is moved up and down (on the Z direction)

at a fixed X, Y location on the surface. The amplitude and phase are recorded as a function of the vertical displacement of the piezo actuator holding the sample. For thermoplastic elastomers, due to the dominant repulsive regime, the recorded difference is only related to the difference in the slopes of the curves, thus in turn to changes of the local mechanical properties. This difference corresponds to the change in the indentation depth. When applied to various polymer systems such as polymer blends and nanocomposites, this technique has been successfully used for distinguishing pure topographic or pure mechanical contrast, as well as intermediate situations with a mixing of the two contributions to the SFM images.[41]

Since SFM can probe local surface mechanical properties with high spatial resolution, down to a few nanometers, and with fine control over the applied force, down to several piconewtons,[42] it represents the ideal set-up to investigate the mechanical properties of many polymeric systems, in particular for systems expected to exhibit nanoscale heterogeneous modulus distribution. In this way properties such as excluded volume effects, strength, elongation, elastic modulus, toughness and elasticity can be studied.[38,43–45] Historically, the elasticity has been probed by SFM exploiting the indentation method,[46,47] in which the SFM tip is pushed into the surface of the sample, and force–distance curves are recorded, providing quantitative insight into elastic properties. However a large indentation with a sharp tip in the sample may break its stress–strain linearity, or even make it fracture. Alternatively the sample elasticity can be studied by SFM phase imaging[48,49] and the force modulation technique.[50] Nevertheless those approaches also have significant limitations. SFM phase imaging can only provide qualitative information about the sample viscoelasticity. The force modulation technique cannot be used on soft samples since during scanning there is a significant lateral force applied to the sample which might alter the sample surface. In the presence of significant adhesion, the force modulation method is no longer quantitative because the elasticity value is derived using the value of applied force, which is difficult to estimate. Marti and co-workers proposed the Pulsed Force Mode (PFM) that extends the use of SFM from the simple imaging of topography to measuring elastic, electrostatic and adhesive sample properties. Due to the intermittent nature of the tip–sample contact, a broad variety of sample surfaces, both delicate and robust, can be studied. Besides the possibility of imaging high material contrasts such as local stiffness and adhesion, the main advantages of the PFM are that there is virtually no lateral force damage and there is precise control of the normal force, so imaging of soft samples is easily possible.[51,52]

Nanoscopic mechanical response

The potential of SFM-based approaches is best expressed when exploring single nanoscale objects, such as isolated polymer chains. The contour of a polymer chain is typically described by making use of a model developed by polymer physicists. One of the most important models is the worm-like chain (WLC) model introduced by Kratky and Porod.[53] It describes a polymer chain with two major parameters: the contour length and the persistence length. Making use of the WLC model, it is possible to quantify properties such as the volume occupied by a random coil formed in solution, which can be measured experimentally by, e.g., light scattering.

The size and mechanical stiffness of isolated polymer chains can also be unveiled by adsorbing the polymer on a flat substrate and imaging it by means of electron microscopy (EM) or SFM. While the former type of studies can be executed only under extremely controlled environmental conditions (i.e., a vacuum), the latter kind of investigations can be done at various interfaces. Therefore they made it possible to also study dynamic processes or behaviors of polymers in their native solutions. By vectorizing the chain contours obtained by microscopy imaging, and making use of a model such as the WLC, it is possible to estimate the contour and persistence lengths of a chain, the latter being the length over which the memory of a chain segment orientation is maintained. Thus it is a way to quantify the stiffness of a polymer chain. This approach was first introduced and exploited on DNA molecules adsorbed at surfaces from data obtained with EM by Frontali et al.,[54] and later by Rivetti et al. on SFM results.[55] More recently this type of investigation has also been performed on synthetic macromolecules.[11,56–60]

The major requirement for singling out properties of isolated polymer chains from EM or SFM images of single strands adsorbed at surfaces is chain equilibration at surfaces.[55] In fact it is most important to note that the chains may be physisorbed on the surface in either a kinetically-trapped 3D conformation or a conformation that is in the 2D thermodynamic equilibrium conformation. In the former case, the observed structures resemble the projection on the surface of the conformations present in solution and reflect the history of the approach of the molecules to the surface. In the latter case, the molecules are allowed to search among their accessible states in two dimensions before they are captured in a particular 2D conformation. Recently it has been shown that simple adsorption of brush-like macromolecules can induce not only conformational deformations but also spontaneous rupture of covalent bonds in the macromolecular backbone, due to the fact that the attractive interaction between the side chains and the substrate is maximized by the spreading of the side chains, which in turn induces tension along the polymer backbone.[61]

Only for chains which are equilibrated at surfaces in quasi 2D, it is possible from SFM or EM images to evaluate quantitatively the persistence length according to the WLC model, and consequently the 3D mechanical and structural properties of the polymer. Therefore, for estimating persistence properties of single polymers when adsorbed at surface it is crucial to be able to differentiate between trapped 3D conformations and macromolecules equilibrated in quasi 2D. This identification can be done using different approaches, as discussed in ref. 55 and 60

The statistical analysis of the curvature of isolated polymeric chains of poly(isocyanodipeptides) (PICs) equilibrated in quasi 2D on the basal plane of mica surfaces revealed that the chains possess a persistence length $\mathscr{L}_p$ of 76 nm (Fig. 4). This indicates that these single polymer molecules are very rigid, i.e., even more rigid than double-stranded DNA. This rigidity was attributed to the helical structure of the polymer
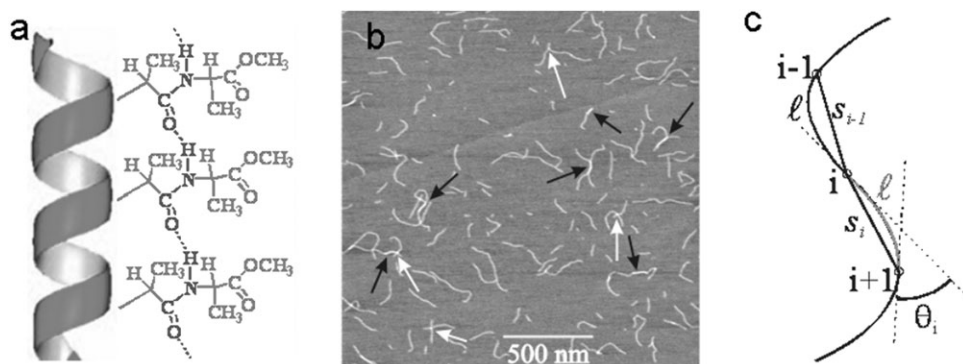
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Fig. 4 (a) Structure of poly(isocyano-L-alanine-D-alanine methyl ester) (PIC) showing the hydrogen-bonded array within the side chains of the polymer. (b) TM-SFM image of a PIC sample. Film prepared from a chloroform solution containing 0.01 g L^{-1} of PIC–Ni. White arrows indicate intersections of separate chains and black ones mark segments consisting of intercoiled chains. Z range = 2 nm. (c) Schematic representation of the determination of θ_i along a chain section of length $\mathscr{L}$ (in gray) which goes from i to $i + 1$. Reprinted with permission from P. Samorí, C. Ecker, I. Gössl, P. A. J. de Witte, J. J. L. M. Cornelissen, G. A. Metselaar, M. B. J. Otten, A. E. Rowan, R. J. M. Nolte and J. P. Rabe, *Macromolecules*, 2002, **35**, 5290. Copyright 2002 American Chemical Society.[60]

backbone and, in particular, to the hydrogen-bond networks that are present between the alanine moieties in the side chains.[60] This result is extremely important since these molecular systems are very versatile objects from a synthetic view point, to the extent that chromophores such as perylenes can be grafted in the peripheral positions, leading to very stiff macromolecules which are expected to act as synthetic antennas; the optical properties of these building blocks were elucidated by making use of confocal optical microscopy.[62] Moreover this slightly hydrophilic macromolecule, in view of its shape persistence, is a nice playground for exploring *in situ* the dynamic swelling of a polymer chain by following its height evolution in different environments, *i.e.*, at various relative humidity and in the presence of CHCl$_3$ vapor.[25]

Despite its great potential, this approach of single polymer experiments is still not well established. This might be due to the difficulties of single molecule experiments, and also to the lack of theoretical knowledge about the conformations of adsorbed chains, which have not been studied systematically so far. In particular, it is not known which conditions lead to chains equilibrated at surfaces. There is an urgent need for methodologies and models to achieve quantitative characterization of the conformation of isolated polymer chains from SFM images.

It is also worth noting that such investigations, relying on a statistical analysis, average over a heterogeneous population pool of data. Making use of SFM it is also possible to address the mechanical response of individual polymer chains. This can be done by attaching a single chain either to the substrate or to the SFM tip, and lifting the tip away from the substrate, thereby stretching the polymer. While in the relaxed state the polymer tends to adopt a coiled conformation due to the maximization of the entropy of its segments, upon extension the macromolecule generates an opposing force because of the entropy decrease. Small extensions need a small force; however, the resistance to the extension increases as the polymer approaches its stretched conformation. The WLC describes the mechanical behaviour of the polymer under this type of stress well.[63,64]

Such single molecule experiments offer insight into the distribution of the experimental observables. This makes it possible to single out sub-states which are commonly averaged out in macroscopic investigations. For example it has been shown, first on the muscle protein titin,[65] and later on other multi-domain proteins, that the different modules constituting the protein can be unfolded one by one. The so-obtained force curve is characterized by a saw-tooth pattern with a number of peaks corresponding to the domains that have been unfolded.[66,67] The possibility of tuning the constant pulling rate and the temperature of the system allows attainment of a thermodynamic quasi-equilibrium condition and to discern between the enthalpy and entropy contribution, respectively.[68,69] Alternatively, making use of the Jarzynski equality relating the irreversible work to the equilibrium free energy difference ΔG, one can obtain equilibrium thermodynamic parameters from processes carried out arbitrarily far from the equilibrium.[70]

This approach has been recently employed also on synthetic polymers to gain, through force distance curves, quantitative information on the elasticity of single macromolecules in solution, on conformational transitions along the chains, about the mechanical stability of chemical bonds and on secondary structures, as well as on the desorption of individual polymer molecules from solid substrates.[71,72] In an early work on a synthetic polyelectrolyte, *i.e.*, poly(methacrylic acid), Ortiz and Hadziioannou demonstrated that the nature of the deformation induced by the tip pulling the polymer strand is solely entropic, also enabling the estimation of the statistical segment and persistence lengths.[42] Such methodology also enables the unveiling of the admolecule–substrate interactions and the singling out of different types of scenarios, including loops, trains or tails of a polymer molecule adsorbed on a surface.[73]

Along the same line, the properties of poly(acrylic acid) (PAA) chains preadsorbed onto a silicon nitride tip surface can be studied and tuned by systematically changing an experimental parameter, such as the pH.[74] To better control the formation of the tip-molecule bond, Gaub and co-workers

have introduced the stable covalent attachment of polyelectrolyte molecules to the SFM tip, which provides the advantage of performing long-term measurements with the same set of molecules and therefore allows the *in situ* observation of the impact of environmental changes on the adsorption behaviour of individual molecules. Approaching and retracting the tip from the surface, different types of interactions, *e.g.* electrostatic or hydrophobic interactions, that determine the adsorption process could be identified and characterized.[75] The elasticity and adhesion forces of poly(acrylamide) derivatives[76] as well as of amphiphilic and hydrophobic dendronized polymers[77] were found to depend on the solvent, in experiments performed at the solid–liquid interface. Similar measurements were also recently performed on copolymers[78,79] and supramolecular polymers.[80,81] Although other tools with a greater force resolution have been developed in the last decade, including magnetic beads and optical tweezers, the practical advantage of force spectroscopy is its greater versatility and its ability to get a 3D picture of the nano-object under investigation.[82]

Conjugated (co)polymers and supramolecular polymers

The optical and electrical properties of materials based on π-conjugated (macro)molecules depend on the structural order within the organic active layer, which needs to be tuned depending on the intended application. For instance, strong interchain interactions are desired within the active layer of field-effect transistors (*i.e.*, at a distance between conjugated units belonging to adjacent chains between 0.3 and 0.4 nm) with the stacking direction of the chains parallel to the substrate plane to give efficient charge transport (high charge carrier mobility).[83] For light-emitting diodes however, strong interchain interactions are undesired, because they usually strongly shift the luminescence spectrum (compared to the solution spectrum) and reduce the quantum yield. Therefore, strategies have been developed to 'isolate' the conjugated backbones from each other by the use of, *e.g.*, bulky side groups,[84,85] cyclodextrin rings[86] and nanochannels[87] to encapsulate macromolecules. For photovoltaic diodes, the ideal active layer consists of a co-continuous network made of electron-donating and electron-accepting materials phase-segregated in the 10 nm range domain (*i.e.*, the typical exciton diffusion length in conjugated polymers).[88] In all cases, "engineering" the supramolecular organization of macromolecules in the solid state plays a key role in controlling the device properties. SPMs are central tools in that study since they allow the elucidation of the molecular packing of conjugated species onto defined surfaces (electrodes, alignment layer, *etc.*) down to the 1–3 nm scale.

Homopolymers and block copolymers

π–π interchain interactions can be employed as the major driving force to self-assemble conjugated macromolecules into specific structures, for instance 1D 'fibrillar' structures. This was first demonstrated by tapping mode SFM studies on thin deposits of hexyl-substituted poly(*para*-phenylene ethynylene) (PPE):[27] the observed 1D structures have a molecular cross-

section (*i.e.*, a few to few tens of nm) and a length of several micrometers, reflecting a ribbon-like shape, see Fig. 5. This nanoribbon morphology is the signature of π–π stacked chains, where the molecular axes are parallel to each other, perpendicular to the stacking direction. In some cases, the ribbons have a thickness of a few molecules packed perpendicularly to the substrate with interdigitated alkyl side groups. This type of ordering into fibrillar structures, which is primarily governed by intermolecular interactions,[89] has been observed in many systems, for instance poly(3-alkylthiophene),[90] and poly(9,9'-dioctylfluorene).[91] Interestingly, this 1D aggregation can also be obtained with conjugated discotic molecules (2D systems), such as phthalocyanines,[92] and conjugated dendrimers (3D systems) made of phenylene units.[93]

In addition to π–π interactions, different weak interactions, including metal complexation and H-bonds can be used to form functional architectures as 1D supramolecules with a molecular cross-section, which can be directly investigated with SFM.[94,95]

Metal–ligand interactions were used to boost the growth into ribbons from a conjugated polymer by grafting crown ethers to poly(*para*-phenylene vinylene) chains. The π–π stacking is assisted by the interactions between the crown ethers in the presence of K^+, and the length of the nanoribbons increases with the standing time of the PPV/K^+ solution.[96]

Recently, "rod-coil" copolymers, which are block copolymers combining a conjugated segment and a non-conjugated segment, have received particular attention,[97] because of the peculiar morphologies arising from the phase separation between the blocks in the solid state, as for instance mushroom-shape aggregates,[98] and microporous hollow micelles.[99] Similarly to what has been observed for conjugated homopolymers, it has also been found that these "rod-coil" macromolecules self-assemble into nanoribbons.[100,101] Nanoribbons form with block copolymers based on conjugated PPE, poly(*para*-phenylene) (PPP), or poly(fluorene) (PF) segments covalently linked to flexible chains, such as poly(ethylene oxide) (PEO) chains (Fig. 5).[102,103] In these copolymers, the nanoscopic morphology can be tuned by varying the block relative volume ratio: with PF–PEO copolymers for instance, the fibrillar morphology survives up to an relative volume ratio of 0.3 in PEO, beyond which nm-thick platelets or μm-sized untextured polymer aggregates form, due to the assembly of PEO chains, which prevents π–π interactions from taking place.[104]

These nanoribbons made of conjugated blocks surrounded by non-conjugated segments can be seen as "insulated supramolecular wires".[105] For example, the nanoribbons can be deposited between source and drain electrodes in a field-effect transistor device and their charge transport properties can be measured, providing a good model for the study of 1D interchain charge transport. The electrical transport properties in these nanowires could also be explored using Conducting Probe Atomic Force Microscopy (CP-AFM), a powerful technique to study nm-size organic structures, which are usually too resistive to be studied by STM.[106] This technique also allows one to execute current–tip voltage measurements at specific locations on the structures, thereby providing direct

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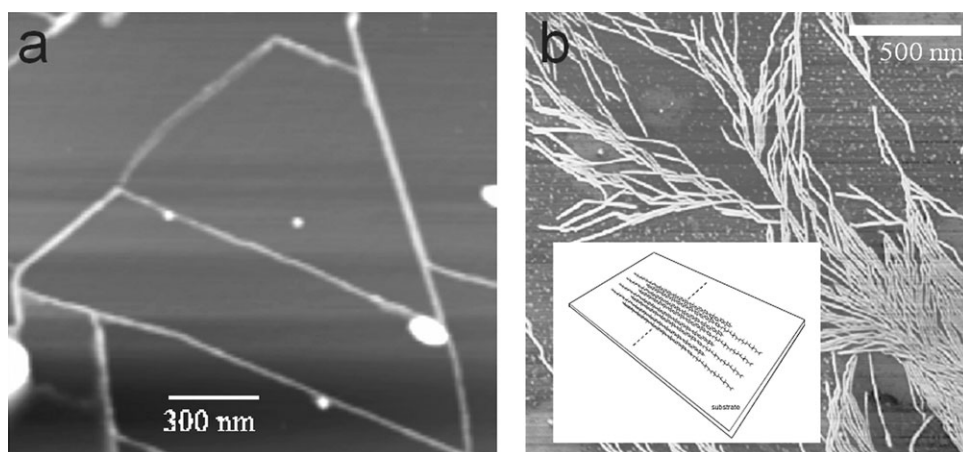*Phys. Chem. Chem. Phys.*, 2006, **8**, 3927–3938 | 3933

Fig. 5 Tapping mode SFM images of ultrathin films of (a) poly(*para*-phenylene ethynylene) (PPE) forming supramolecular nanoribbons adsorbed on mica[108] and of (b) poly(ethylene oxide)-poly(fluorene)-poly(ethylene oxide) triblock copolymer $(EO)_{45}$-$(F)_{20}$-$(EO)_{45}$ on mica. Inset: Model of packing of the model system, *i.e.*, $(F)_8$-$(EO)_8$, into fibrillar structures. (Left) Reprinted from *Thin Solid Films*, **336**, P. Samorí, V. Francke, K. Müllen and J. P. Rabe, Growth of solution cast macromolecular π-conjugated nanoribbons on mica, pp. 13–15, copyright 1998, with permission from Elsevier.[108] (Right) Reprinted from M. Surin, D. Marsitzky, A. C. Grimsdale, K. Müllen, R. Lazzaroni and Ph. Leclère, *Adv. Funct. Mater.*, 2004, **14**, 708, with permission from Wiley VCH.[104]

electrical measurements of defects, such as grain boundaries or kinks in the wires, that could act as bottle-necks for the charge transport. Moreover, the local electronic properties of nano-scale architectures could be unraveled by Kelvin Probe Force Microscopy by offering quantitative insight into the work function of nanostructures, *e.g.*, providing pathways towards the optimization of the charge injection at the interface between a metallic electrode and a macromolecular nanos-tructure.[107]

Supramolecular polymers and helicity

Helical structures, arising from the supramolecular assembly of chiral or non-chiral molecules, are very appealing to scientists, not only because of their esthetics but also because such structural motifs are abundantly found in nature in many biopolymers. Helices also exhibit some unique properties like their shape and optical anisotropy and mechanical strength, which makes them attractive objects for novel nanoarchitec-tures and hierarchically organized materials.[109] Nevertheless, and despite the progress in supramolecular science, the mole-cular design of dynamic self-assembling helices with pre-defined periodicity and dimensions remains a huge challenge that has to be addressed in order to fully benefit from the unique properties of helices. Controlling the curvature is essential for the construction of well-defined objects,[110,111] and in the case of helices there is a direct relationship between helical curvature, periodicity (p, helical pitch), and the radius (r). With the advent of SFM it is now possible to investigate more closely, at the atomic level, the architecture of the chiral nano-objects and to gain insight into their mechanical proper-ties. Helices are also unique in the way they assemble: due to the build up of curvature, they form finite bundles and not infinite bundles as seen for non-chiral fibers and linear rods.

Meijer and co-workers have thoroughly developed a series of 1D 'supramolecular polymers', *i.e.*, small molecules inter-acting through non-covalent forces and forming long chains,

based on conjugated moieties carrying chiral groups, which assemble in solution into helical structures owing to the inter-play between terminal H-bond motifs between two moieties, and π-stacking along the axis of the column.[112,113] Recently, they transferred such helical columnar stacks made of H-bonded oligo(phenylenevinylene) (OPV) bearing chiral alkoxy side-groups from solution onto defined substrates, in the frame of applications in supramolecular electronics. By SFM, they showed that isolated cylinders are observed only if specific concentrations and specific solid supports are chosen; in the best conditions, isolated cylinders have an average shape persistence of about 125 nm, a parameter which could be compared to the persistence length of single polymer chains.[114] Their results are in line with observations of supramolecular structures formed directly on surfaces (*i.e.*, not pre-formed in solution but starting from a solution in which the molecules are isolated): oligothiophenes end-substituted with chiral oli-go(ethylene oxide) groups form left-handed chiral 1D supra-molecular architectures, extending over several μm, only on substrates of intermediate polarity (*e.g.*, silicon oxide, glass), while deposits on either non-polar (graphite) or strongly polar (mica) substrates reveal non-chiral well-ordered aggre-gates.[115,116] Very interestingly, a very recent SFM study revealed that both left-handed and right-handed helical cylin-ders can be obtained from the stacking of only one enantiomer OPV ("S" compound, or in mixed stacks with non-chiral OPV) when the stacks are deposited on mica.[117]

Despite recent progress, at this stage there is very little understanding about how chiral molecules self-assemble onto non-chiral surfaces, which is a key point for the chirality to be expressed at the supramolecular level in the solid state.

Helicity can also be induced at the single chain level by placing chiral groups and/or by steric constraints along the chains.[118] This is the case for instance with poly(phenylacety-lene)s, which adopt a helical conformation provided that chiral pendants groups are present. With non-chiral substitu-ents, a one-handed helicity can also be obtained using small,

optically-active molecules capable of complexing the polymer chains, as suggested by SFM studies by Yashima and collaborators.[119] They also showed that rigid-rod helical poly(phenylacetylene)s bearing L- or D-alanine residues exposing a long alkyl chain self-assemble into ordered hierarchical 2D crystals under exposure of solvent vapors on HOPG. First, flat monolayers immediately and epitaxially form on the basal plane of graphite, on which rod-like helical polyacetylenes further self-assemble into 2D helix-bundles with controlled helicity upon exposure of organic solvents. High-resolution SFM revealed their helical conformations in the 2D crystals and enabled the determination of the molecular packing, helical pitch and handedness. These values agree well with those determined by X-ray diffraction of the oriented liquid crystalline polymer films.[120] The control and fabrication of the 2D molecular ordering of chiral (macro)molecules on substrates is among the great challenges in materials science, due to attractive applications in chemical sensing, electro-optical devices, enantioselective adsorbents and catalysis.[95]

All together, these results pave the way towards new approaches not only for the construction of new chiral materials, such as chiral selectors and catalysts, but also for the rational design of novel switchable chiral surfaces based on inversion of helicity of macromolecules.[118,121–126]

If helical architectures based on single components are already a great challenge, the formation of helical motifs from more than one component is even more difficult. Rabe and Schlüter recently showed that mastering electrostatic interactions between macromolecules is a route to designing helical supramolecular architectures by mixing synthetic and biologi-cal polymers.[127] This was demonstrated on positively-charged dendronized polymers (with protonated amine groups at the periphery and different dendron generations) which were found to be able to complex with DNA, forming cylindrically shaped nano-objects. SFM provided evidence for the behaviour of DNA to wrap around the dendronized polymers, see Fig. 6. For the different dendron generations, it was proposed that the interplay between the electrostatic energy and elastic energy defines both the overall charge of the complex and the different pitch sizes for the wrapped DNA. The dendronized polymers together with DNA are a useful model system to test theories on the interaction of oppositely-charged polyelectrolytes. Moreover, this novel complex might be used for nonviral gene delivery systems and help to optimize the transfection efficiency based on the structure of the vector system.[127]

Many questions arise, such as: (i) How is molecular chirality expressed at the supramolecular level? (ii) How strong is a helical nanospring? Can its behavior be described with the Hooke's law? (iii) How are the mechanical properties transferred from a single molecule nanospring to a finite bundle of helices? These open issues are just a few of the questions that might be tackled in future SFM studies of helical nanostructures.

Conclusions and outlook

Scanning force microscopies (SFMs) are indisputably a fundamental tool for the study of physico-chemical properties of polymer-based architectures. Their capability of providing direct insight beyond imaging, along with the versatility of the techniques allowing the study of molecular based materials under a variety of environmental conditions, pave the way towards the optimization of functional materials and finally open up a vast range of applications that foster materials science into the nanoscale world.

The exploration of very small objects, such as single polymer chains, will require in the years to come the improvement of the spatial resolution, which can be foreseen to be facilitated by the development of new application modes and/or enhanced properties of the present set-ups, including the tips. More and more applications of nanomanipulation by means of SFM can be foreseen, as a way to cast light onto the mechanics of single nano-objects as well as for the construction of complex architectures, perhaps not thermodynamically favored.

To control the processability of macromolecules into given nano-objects at surfaces requires a careful consideration of the molecule–molecule interactions. For this, the excluded volume of a polymer, *i.e.*, the volume from which a macromolecule in a solution effectively excludes all other segments both belonging to the same or other macromolecules, represents a truly important parameter since it is known that the polymer chains adopt a different conformation in bad and good solvents, *i.e.*, when coiled and swollen, respectively. Flory's theta solvent marks the boundary between the good and bad solvents, as in a theta solvent the macromolecules adopt their unperturbed dimensions. In other words the shape of molecules in a pure melt should be the same as under theta conditions. In the theta solvent, the medium provides an exact compensation for the
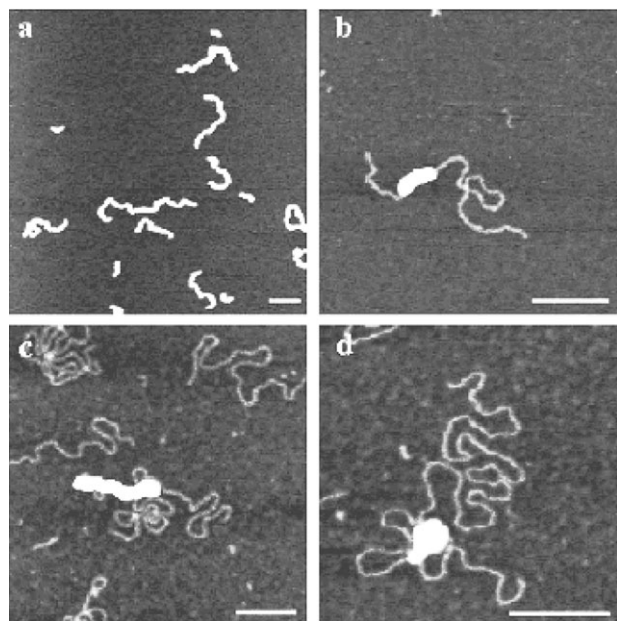

Fig. 6 High-resolution SFM images of (a) fourth-generation dendronized polymer (PG4) deposited onto freshly cleaved mica. (b–d) DNA–PG4 complexes of charge ratio 1 : 0.7 precipitated onto poly-L-ornithine-coated mica. The scale bars represent 250 nm. Reprinted with permission from I. Gössl, L. J. Shu, A. D. Schlüter and J. P. Rabe, *J. Am. Chem. Soc.*, 2002, **124**, 6860. Copyright 2002 American Chemical Society.[127]

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excluded volume effect. In essence, the theta solvent can be considered the reference solvent type for the chosen macromolecules to be processed from solution at surfaces. Using such solvent processing conditions is thus expected to provide control over the organization of macromolecules at surfaces.

In certain cases, in particular for large molecules with a strong tendency to aggregate, poor solubility might be a limiting factor, not only for the processing from solution, but also for the purification of the compounds after synthesis. Nevertheless, the possibility of handling larger and larger molecules provides access to increasingly complex functions.[1,128–130] Unfortunately, larger molecules commonly imply lower processability due to either their low solubility in liquid media or the occurrence of thermal cracking during vacuum sublimation. The search for novel strategies to process and characterise giant building blocks is therefore a crucial goal in materials science. Very recently, a new general route to process extraordinarily large molecules at surfaces, potentially including polymers, into ultra-pure crystalline architectures has been introduced. Such a method relies on the soft-landing of ions[131] generated by solvent-free matrix assisted laser desorption/ionization (MALDI). Giant molecules have been transferred to the gas phase, purified and adsorbed at surfaces into crystalline architectures. The unique flexibility of this approach allows the growth of ultra-pure crystalline films of various systems, such as organic, inorganic and biological molecules. Therefore it can be of interest for technological applications in the fields of electronics, (bio)catalysis and nanomedicine.[132]

The rapidly expanding and highly dynamic character of the use of SFM approaches on polymers means that it was impossible to cover all the detailed aspects in this review. This represents a demonstration of the potential of this methodology for both innovation and breakthroughs. Indeed, although SFM is nowadays an established tool for mapping polymeric surfaces, its use beyond imaging is still in its infancy.[133] As the relationship between molecular building blocks and architecture and ultimately function is more fully understood, self-organization of polymers into supramolecular functional materials will inevitably become less of an art, and more of an exact science. The precise control over the functionality in supramolecular polymeric architectures opens avenues for the fabrication of prototype nanoscale and macroscopic devices with tailor-made functions, with potential future applications in the fields of nanoelectronics, optoelectronics and data-storage.

Acknowledgements

References

1 Special issue on Supramolecular chemistry and self-assembly, , *Science*, 2002, **295**, p. 2395.
2 J. A. A. W. Elemans, A. E. Rowan and R. J. M. Nolte, *J. Mater. Chem.*, 2003, **13**, 2661.
3 A. C. Grimsdale and K. Müllen, *Angew. Chem., Int. Ed.*, 2005, **44**, 5592.
4 Special issue on Supramolecular Approaches to Organic Electronics and Nanotechnology, , *Adv. Mater.*, 2006, **18**, p. 1227.
5 G. Binnig, H. Rohrer, C. Gerber and E. Weibel, *Appl. Phys. Lett.*, 1982, **40**, 178.
6 P. Samorí, *J. Mater. Chem.*, 2004, **14**, 1353.
7 J. Loos, *Adv. Mater.*, 2005, **17**, 1821.
8 G. Binnig, C. F. Quate and C. Gerber, *Phys. Rev. Lett.*, 1986, **56**, 930.
9 P. Samorí, *Chem. Soc. Rev.*, 2005, **34**, 551.
10 H. Takano, J. R. Kenseth, S.-S. Wong, J. C. O'Brien and M. D. Porter, *Chem. Rev.*, 1999, **99**, 2845.
11 S. Sheiko and M. Möller, *Chem. Rev.*, 2001, **101**, 4099.
12 G. J. Vancso, H. Hillborg and H. Schonherr, *Polymer Analysis, Polymer Theory*, 2005, **vol. 182**, p. 55.
13 Q. Zhong, D. Innis, K. Kjoller and V. B. Elings, *Surf. Sci. Lett.*, 1993, **290**, L688.
14 T. R. Albrecht, P. Grütter, D. Horne and D. Rugard, *J. Appl. Phys.*, 1991, **69**, 668.
15 J. Barner, F. Mallwitz, L. J. Shu, A. D. Schlüter and J. P. Rabe, *Angew. Chem., Int. Ed.*, 2003, **42**, 1932.
16 A. P. Alivisatos, P. F. Barbara, A. W. Castleman, J. Chang, D. A. Dixon, M. L. Klein, G. L. McLendon, J. S. Miller, M. A. Ratner, P. J. Rossky, S. I. Stupp and M. E. Thompson, *Adv. Mater.*, 1998, **10**, 1297.
17 P. Samorí, M. Keil, R. Friedlein, J. Birgerson, M. Watson, M. Müllen, W. R. Salaneck and J. P. Rabe, *J. Phys. Chem. B*, 2001, **105**, 11114.
18 P. Samorí, H. Engelkamp, P. A. J. de Witte, A. E. Rowan, R. J. M. Nolte and J. P. Rabe, *Adv. Mater.*, 2005, **17**, 1265.
19 A. Pallandre, B. De Meersman, F. Blondeau, B. Nysten and A. M. Jonas, *J. Am. Chem. Soc.*, 2005, **127**, 4320.
20 R. Garcia, M. Tello, J. F. Moulin and F. Biscarini, *Nano Lett.*, 2004, **4**, 1115.
21 J. Tamayo and R. Garcia, *Langmuir*, 1996, **12**, 4430.
22 C. Bustamante and D. Keller, *Phys. Today*, 1995, **48**, 32.
23 J. Kumaki, T. Kawauchi and E. Yashima, *Macromolecules*, 2006, **39**, 1209.
24 H. Xu, D. Shirvanyants, K. Beers, K. Matyjaszewski, M. Rubinstein and S. S. Sheiko, *Phys. Rev. Lett.*, 2004, **93**.
25 W. Zhuang, C. Ecker, G. A. Metselaar, A. E. Rowan, R. J. M. Nolte, P. Samorí and J. P. Rabe, *Macromolecules*, 2005, **38**, 473.
26 A. Rudin, *The Elements of Polymer Science and Engineering: An Introductory Text and Reference for Engineers and Chemists*, Academic Press, San Diego, CA, 1990.
27 P. Samorí, V. Francke, K. Müllen and J. P. Rabe, *Chem.-Eur. J.*, 1999, **5**, 2312.
28 S. S. Sheiko, M. da Silva, D. Shirvaniants, I. LaRue, S. Prokhorova, M. Möller, K. Beers and K. Matyjaszewski, *J. Am. Chem. Soc.*, 2003, **125**, 6725.
29 M. Severin, J. Barner, A. A. Kalachev and J. P. Rabe, *Nano Lett.*, 2004, **4**, 577.
30 P. Samorí, J. J. J. M. Donners, N. Severin, M. B. J. Otten, A. P. Rabe, R. J. M. Nolte and N. A. J. M. Sommerdijk, *Langmuir*, 2004, **20**, 8955.
31 D. M. Price, M. Reading, A. Hammiche and H. M. Pollock, *Int. J. Pharm.*, 1999, **192**, 85.
32 S. Sills and R. M. Overney, *Phys. Rev. Lett.*, 2003, **91**.
33 F. Dinelli, C. Buenviaje and R. M. Overney, *J. Chem. Phys.*, 2000, **113**, 2043.
34 K. Tanaka, A. Takahara and T. Kajiyama, *Macromolecules*, 2000, **33**, 7588.
35 O. K. C. Tsui, X. P. Wang, J. Y. L. Ho, T. K. Ng and X. D. Xiao, *Macromolecules*, 2000, **33**, 4198.

36 K. Tanaka, K. Hashimoto, T. Kajiyama and A. Takahara, *Langmuir*, 2003, **19**, 6573.

37 T. Kajiyama, K. Tanaka, I. Ohki, S. R. Ge, J. S. Yoon and A. Takahara, *Macromolecules*, 1994, **27**, 7932.

38 B. Y. Du, O. K. C. Tsui, Q. L. Zhang and T. B. He, *Langmuir*, 2001, **17**, 3286.

39 S. Kopp-Marsaudon, Ph. Leclère, F. Dubourg, R. Lazzaroni and J. P. Aimé, *Langmuir*, 2000, **16**, 8432.

40 Ph. Leclère, F. Dubourg, S. Kopp-Marsaudon, J. L. Brédas, R. Lazzaroni and J. P. Aimé, *Appl. Surf. Sci.*, 2002, **188**, 524.

41 Ph. Leclère, P. Viville, M. Jeusette, J. P. Aimé and R. Lazzaroni, in *Scanning Probe Microscopies beyond imaging-Manipulation of Molecules and Nanostructures*, ed. P. Samorí, Wiley-VCH, Weinheim, 2006, p. 175.

42 C. Ortiz and G. Hadziioannou, *Macromolecules*, 1999, **32**, 780.

43 J. Domke and M. Radmacher, *Langmuir*, 1998, **14**, 3320.

44 D. C. Hurley, K. Shen, N. M. Jennett and J. A. Turner, *J. Appl. Phys.*, 2003, **94**, 2347.

45 A. Touhami, B. Nysten and Y. F. Dufrene, *Langmuir*, 2003, **19**, 4539.

46 J. Fraxedas, S. Garcia-Manyes, P. Gorostiza and F. Sanz, *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 5228.

47 E. Tomasetti, R. Legras and B. Nysten, *Nanotechnology*, 1998, **9**, 305.

48 P. Leclère, R. Lazzaroni, J. L. Brédas, J. M. Yu, P. Dubois and R. Jérôme, *Langmuir*, 1996, **12**, 4317.

49 M. O. Finot and M. T. McDermott, *J. Am. Chem. Soc.*, 1997, **119**, 8564.

50 J. S. Jourdan, S. J. Cruchon-Dupeyrat, Y. Huan, P. K. Kuo and G. Y. Liu, *Langmuir*, 1999, **15**, 6495.

51 A. RosaZeiser, E. Weilandt, S. Hild and O. Marti, *Meas. Sci. Technol.*, 1997, **8**, 1333.

52 H. U. Krotil, T. Stifter, H. Waschipky, K. Weishaupt, S. Hild and O. Marti, *Surf. Interface Anal.*, 1999, **27**, 336.

53 O. Kratky and G. Porod, *Recl. Trav. Chim. Pays-Bas*, 1949, **68**, 1106–1122.

54 C. Frontali, E. Dore, A. Ferrauto and E. Gratton, *Biopolymers*, 1979, **18**, 1353–1373.

55 C. Rivetti, M. Guthold and C. Bustamante, *J. Mol. Biol.*, 1996, **264**, 919.

56 E. Balnois, S. Stoll, K. J. Wilkinson, J. Buffle, M. Rinaudo and M. Milas, *Macromolecules*, 2000, **33**, 7440.

57 A. Kiriy, G. Gorodyska, S. Minko, W. Jaeger, P. Stepanek and M. Stamm, *J. Am. Chem. Soc.*, 2002, **124**, 13454.

58 T. A. Camesano and K. J. Wilkinson, *Biomacromolecules*, 2001, **2**, 1184.

59 P. G. Khalatur, A. R. Khokhlov, S. A. Prokhorova, S. S. Sheiko, M. Moller, P. Reineker, D. G. Shirvanyanz and N. Starovoitova, *Eur. Phys. J. E*, 2000, **1**, 99.

60 P. Samorí, C. Ecker, I. Gössl, P. A. J. de Witte, J. J. L. M. Cornelissen, G. A. Metselaar, M. B. J. Otten, A. E. Rowan, R. J. M. Nolte and J. P. Rabe, *Macromolecules*, 2002, **35**, 5290.

61 S. S. Sheiko, F. C. Sun, A. Randall, D. Shirvanyants, M. Rubinstein, H. Lee and K. Matyjaszewski, *Nature*, 2006, **440**, 191.

62 J. Hernando, P. A. J. de Witte, E. M. H. P. van Dijk, J. Korterik, R. J. M. Nolte, A. E. Rowan, M. F. García-Parajó and N. F. van Hulst, *Angew. Chem., Int. Ed.*, 2004, **43**, 4045.

63 A. Y. Grosberg and A. R. Khokhlov, *Statistical Physics of Macromolecules*, AIP Press, New York, 1994.

64 C. Bustamante, J. F. Marko, E. D. Siggia and S. Smith, *Science*, 1994, **265**, 1599.

65 M. Rief, M. Gautel, F. Oesterhelt, J. M. Fernandez and H. E. Gaub, *Science*, 1997, **276**, 1109.

66 T. E. Fisher, A. F. Oberhauser, M. Carrion-Vazquez, P. E. Marszalek and J. M. Fernandez, *Trends Biochem. Sci.*, 1999, **24**, 379.

67 R. B. Best and J. Clarke, *Chem. Commun.*, 2002, 183.

68 B. Samorí, *Chem.-Eur. J.*, 2000, **6**, 4249.

69 S. Zepeda, Y. Yeh and A. Noy, *Langmuir*, 2003, **19**, 1457.

70 J. Liphardt, S. Dumont, S. B. Smith, I. Tinoco and C. Bustamante, *Science*, 2002, **296**, 1832.

71 T. Hugel and M. Seitz, *Macromol. Rapid Commun.*, 2001, **22**, 989.

72 W. Zhang and X. Zhang, *Prog. Polym. Sci.*, 2003, **28**, 1271.

73 M. Conti, Y. Bustanji, G. Falini, P. Ferruti, S. Stefoni and B. Samorí, *ChemPhysChem*, 2001, **2**, 610.

74 L. Sonnenberg, J. Parvole, O. Borisov, L. Billon, H. E. Gaub and M. Seitz, *Macromolecules*, 2006, **39**, 281.

75 C. Friedsam, M. Seitz and H. E. Gaub, *J. Phys.: Condens. Matter*, 2004, **16**, S2369.

76 C. Wang, W. Q. Shi, W. K. Zhang, X. Zhang, Y. Katsumoto and Y. Ozaki, *Nano Lett.*, 2002, **2**, 1169.

77 W. Q. Shi, Z. Q. Wang, S. X. Cui, X. Zhang and Z. S. Bo, *Macromolecules*, 2005, **38**, 861.

78 D. Zhang and C. Ortiz, *Macromolecules*, 2005, **38**, 2535.

79 D. Zhang and C. Ortiz, *Macromolecules*, 2004, **37**, 4271.

80 S. Zou, H. Schonherr and G. J. Vancso, *Angew. Chem., Int. Ed.*, 2005, **44**, 956.

81 S. Zou, H. Schonherr and G. J. Vancso, *J. Am. Chem. Soc.*, 2005, **127**, 11230.

82 C. Bustamante, J. C. Macosko and G. J. L. Wuite, *Nat. Rev. Mol. Cell Biol.*, 2000, **1**, 130.

83 H. Sirringhaus, P. J. Brown, R. H. Friend, M. M. Nielsen, K. Bechgaard, B. M. W. Langeveld-Voss, A. J. H. Spiering, R. A. J. Janssen, E. W. Meijer, P. Herwig and D. M. de Leeuw, *Nature*, 1999, **401**, 685.

84 A. C. Grimsdale, Ph. Leclère, R. Lazzaroni, J. D. Mackenzie, C. Murphy, S. Setayesh, C. Silva, R. H. Friend and K. Müllen, *Adv. Funct. Mater.*, 2002, **12**, 729.

85 M. Surin, E. Hennebicq, C. Ego, D. Marsitzky, A. C. Grimsdale, K. Müllen, J. L. Brédas, R. Lazzaroni and Ph. Leclère, *Chem. Mater.*, 2004, **16**, 994.

86 F. Cacialli, J. S. Wilson, J. J. Michels, C. Daniel, C. Silva, R. H. Friend, N. Severin, P. Samorí, J. P. Rabe, M. J. O'Connell, P. N. Taylor and H. L. Anderson, *Nat. Mater.*, 2002, **1**, 160.

87 J. Gierschner, H. J. Egelhaaf, H. G. Mack, D. Oelkrug, R. M. Alvarez and M. Hanack, *Synth. Met.*, 2003, **137**, 1449.

88 J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti and A. B. Holmes, *Nature*, 1995, **376**, 498.

89 P. Samorí, I. Sikharulidze, V. Francke, K. Müllen and J. P. Rabe, *Nanotechnology*, 1999, **10**, 77.

90 H. C. Yang, T. J. Shin, L. Yang, K. Cho, C. Y. Ryu and Z. N. Bao, *Adv. Funct. Mater.*, 2005, **15**, 671.

91 J. Chappell, D. G. Lidzey, P. C. Jukes, A. M. Higgins, R. L. Thompson, S. O'Connor, I. Grizzi, R. Fletcher, J. O'Brien, M. Geoghegan and R. A. L. Jones, *Nat. Mater.*, 2003, **2**, 616.

92 A. S. Drager, R. A. P. Zangmeister, N. R. Armstrong and D. F. O'Brien, *J. Am. Chem. Soc.*, 2001, **123**, 3595.

93 D. J. Liu, H. Zhang, P. C. M. Grim, S. De Feyter, U. M. Wiesler, A. J. Berresheim, K. Müllen and F. C. De Schryver, *Langmuir*, 2002, **18**, 2385.

94 F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer and A. Schenning, *Chem. Rev.*, 2005, **105**, 1491.

95 S. De Feyter and F. C. De Schryver, *Chem. Soc. Rev.*, 2003, **32**, 139.

96 Y. H. Luo, H. W. Liu, F. Xi, L. Li, X. G. Jin, C. C. Han and C. M. Chan, *J. Am. Chem. Soc.*, 2003, **125**, 6447.

97 M. Lee, B.-K. Cho and W.-C. Zin, *Chem. Rev.*, 2001, **101**, 3869.

98 S. I. Stupp, V. LeBonheur, K. Walker, L. S. Li, K. E. Huggins, M. Keser and A. Amstutz, *Science*, 1997, **276**, 384.

99 S. A. Jenekhe and X. L. Chen, *Science*, 1999, **283**, 372.

100 E. D. Sone, E. R. Zubarev and S. I. Stupp, *Angew. Chem., Int. Ed.*, 2002, **41**, 1705.

101 E. R. Zubarev, M. U. Pralle, E. D. Sone and S. I. Stupp, *J. Am. Chem. Soc.*, 2001, **123**, 4105.

102 Ph. Leclère, A. Calderone, D. Marsitzky, V. Francke, Y. Geerts, K. Müllen, J. L. Brédas and R. Lazzaroni, *Adv. Mater.*, 2000, **12**, 1042.

103 Ph. Leclère, E. Hennebicq, A. Calderone, P. Brocorens, A. C. Grimsdale, K. Müllen, J. L. Brédas and R. Lazzaroni, *Prog. Polym. Sci.*, 2003, **28**, 55.

104 M. Surin, D. Marsitzky, A. C. Grimsdale, K. Müllen, R. Lazzaroni and Ph. Leclère, *Adv. Funct. Mater.*, 2004, **14**, 708.

105 A. P. H. J. Schenning and E. W. Meijer, *Chem. Commun.*, 2005, 3245.

106 T. W. Kelley, E. L. Granstrom and C. D. Frisbie, *Adv. Mater.*, 1999, **11**, 261.

107 V. Palermo, M. Palma and P. Samorí, *Adv. Mater.*, 2006, **18**, 145.

108 P. Samorí, V. Francke, K. Müllen and J. P. Rabe, *Thin Solid Films*, 1998, **336**, 13.

This journal is © the Owner Societies 2006

Phys. Chem. Chem. Phys., 2006, **8**, 3927–3938 | 3937

109 V. Percec, M. Glodde, T. K. Bera, Y. Miura, I. Shiyanovskaya, K. D. Singer, V. S. K. Balagurusamy, P. A. Heiney, I. Schnell, A. Rapp, H. W. Spiess, S. D. Hudson and H. Duan, *Nature*, 2002, **419**, 384.

110 J. N. Israelachvili, S. Marcelja and R. G. Horn, *Q. Rev. Biophys.*, 1980, **13**, 121.

111 G. A. Ozin, *Can. J. Chem.*, 1999, **77**, 2001.

112 J. H. K. K. Hirschberg, L. Brunsveld, A. Ramzi, J. A. J. M. Vekemans, R. P. Sijbesma and E. W. Meijer, *Nature*, 2000, **407**, 167.

113 A. P. H. J. Schenning, P. Jonkheijm, E. Peeters and E. W. Meijer, *J. Am. Chem. Soc.*, 2001, **123**, 409.

114 P. Jonkheijm, F. J. M. Hoeben, R. Kleppinger, J. van Herrikhuyzen, A. P. H. J. Schenning and E. W. Meijer, *J. Am. Chem. Soc.*, 2003, **125**, 15941.

115 A. P. H. J. Schenning, A. F. M. Kilbinger, F. Biscarini, M. Cavallini, H. J. Cooper, P. J. Derrick, W. J. Feast, R. Lazzaroni, Ph. Leclère, L. A. McDonell, E. W. Meijer and S. C. J. Meskers, *J. Am. Chem. Soc.*, 2002, **124**, 1269.

116 Ph. Leclère, M. Surin, R. Lazzaroni, A. F. M. Kilbinger, O. Henze, P. Jonkheijm, F. Biscarini, M. Cavallini, W. J. Feast, E. W. Meijer and A. P. H. J. Schenning, *J. Mater. Chem.*, 2004, **14**, 1959.

117 A. Ajayaghosh, R. Varghese, S. J. George and C. Vijayakumar, *Angew. Chem., Int. Ed.*, 2006, **45**, 1141.

118 J. Cornelissen, A. E. Rowan, R. J. M. Nolte and N. Sommerdijk, *Chem. Rev.*, 2001, **101**, 4039.

119 S. Sakurai, K. Kuroyanagi, K. Morino, M. Kunitake and E. Yashima, *Macromolecules*, 2003, **36**, 9670.

120 S. I. Sakurai, K. Okoshi, J. Kumaki and E. Yashima, *Angew. Chem., Int. Ed.*, 2006, **45**, 1245.

121 J.-M. Lehn, *Supramolecular Chemistry - Concepts and Perspectives*, VCH, Weinheim, 1995.

122 D. J. Hill, M. J. Mio, R. B. Prince, T. S. Hughes and J. S. Moore, *Chem. Rev.*, 2001, **101**, 3893.

123 M. M. Green, J. W. Park, T. Sato, A. Teramoto, S. Lifson, R. L. B. Selinger and J. V. Selinger, *Angew. Chem., Int. Ed.*, 1999, **38**, 3139.

124 E. Yashima, K. Maeda and T. Nishimura, *Chem.-Eur. J.*, 2004, **10**, 43.

125 T. Nakano and Y. Okamoto, *Chem. Rev.*, 2001, **101**, 4013.

126 L. Brunsveld, B. J. B. Folmer, E. W. Meijer and R. P. Sijbesma, *Chem. Rev.*, 2001, **101**, 4071.

127 I. Gössl, L. J. Shu, A. D. Schlüter and J. P. Rabe, *J. Am. Chem. Soc.*, 2002, **124**, 6860.

128 R. E. Martin, T. Mader and F. Diederich, *Angew. Chem., Int. Ed.*, 1999, **38**, 817.

129 V. Balzani, A. Credi, F. M. Raymo and J. F. Stoddart, *Angew. Chem., Int. Ed.*, 2000, **39**, 3349.

130 M. Van der Auweraer and F. C. De Schryver, *Nat. Mater.*, 2004, **3**, 507.

131 V. Franchetti, B. H. Solka, W. E. Baitinger, J. W. Amy and R. G. Cooks, *Int. J. Mass Spectrom. Ion Phys.*, 1977, **23**, 29.

132 H. J. Räder, A. Rouhanipour, A. M. Talarico, V. Palermo, P. Samorí and K. Müllen, *Nat. Mater.*, 2006, **5**, 276.

133 P. Samorí, *Scanning Probe Microscopies: Beyond Imaging - Manipulation of Molecules and Nanostructures*, Wiley-VCH, Weinheim, 2006.