Part I Preparation 1

1 A Perspective and Introduction to Organic and Polymer Ultrathin Films: Deposition, Nanostructuring, Biological Function, and Surface Analytical Methods

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Monolayer and multilayer ultrathin films of organic, polymeric, and/or hybrid materials have gained much attention over the last several decades owing to their fundamental importance in understanding materials' properties in confined geometries and their potential applications as smart and/or stimuli-responsive coatings, in microelectronics, electro-optics, sensors, nanotechnology, and biotechnology, to mention but a few. Ultrathin films are defined at a scale that is smaller than what can be industrially accessed by spin-casting or roll-to-roll transfer methods for the deposition of coatings. "Ultrathin" usually refers to thicknesses in the submicrometer or even sub-100-nm scale for a coating on a relatively flat solid support or surface. By going to the nanoscale, the main advantage is the ability to control nanostructured architectures in which self-assembly or directed assembly of organic materials are formed as ultrathin films on the substrates. These monolayers may in fact be ordered assemblies themselves that display long-range ordering including crystallinity, liquid crystallinity, nanoscopic, and/or mesoscopic structures. Subsequently, multilayers can be produced by repetitive or alternating "layer-by-layer" deposition of individual monolayers. Thereby, it is possible to control the molecular orientation and organization at the nanoscale thus precisely tuning the macroscopic properties of the organic and polymer thin films. This stacking can be in the form of oriented or isotropic "random" stacking, which can be replicated by self- or directed assembly.

The oldest technique for fabricating multilayer ultrathin films (and the most extensively studied prior to the 1990s) is the formation by the sequential deposition of individual monolayers known as the Langmuir–Blodgett (LB) or Langmuir–Blodgett–Kuhn (LBK) technique. The monolayers are equilibrated at the air/water interface and then transferred onto a solid substrate either by dipping the substrate in a vertical deposition step or by horizontal transfer (Langmuir–Schaefer technique). Multilayers can be realized by repetitive dipping. The LB technique, indeed, provided scientists with the practical capability to construct ordered monomolecular assemblies that can be probed with surface sensitive analytical techniques. However, as many have realized, the LB technique requires special equipment and has severe limitations with respect to substrate size and topology as well as film quality and stability. Another approach to assembling

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layered ultrathin film structures based on chemisorption was also reported widely in the early 1980s. These are called self-assembled monolayers (SAMs) and are usually based on the adsorption of amphiphilic or reactive molecules on specific surfaces thus forming monolayers with a certain degree of thermal stability. Also in the 1980s, multilayer films were reported to be prepared by a two-step sequential reaction protocol of deposition followed by chemical reaction of the end-groups involving, for example, protected-deprotection schemes with silanes and hydroxylated surfaces employing the conversion of a nonpolar terminal group to a hydroxyl group. Once a subsequent monolayer is adsorbed on the "activated" monolayer, multilayer films may be built by repetition of this process. This has also been a route toward inorganic multilayer films, for example, sequential complexation of Zr^{4+} and α,ω -bisphosphonic acid. However, self-assembled films based on covalent or coordination chemistry are restricted to certain classes of organics, and high-quality homogeneous multilayer films or large-area films cannot be reliably obtained because of the high steric demand of covalent chemistry and the requirement for 100% reactivity in each step.

The layer-by-layer deposition of oppositely charged molecules and polyelectrolytes was first reported in the early 1990s. This was a revival of a previous method reported in the 1960s relying mostly on electrostatic attraction. It was the ability to form multilayers with precise control over the total thickness, that is, in the range of a few tenths of nanometers up to micrometers, without the use of the more expensive LB deposition equipment that has allowed this fabrication concept to become the most popular ultrathin film-preparation method to date. This is due to its characteristic repetitive deposition steps, using essentially a "beaker technique" that even a high-school student can play around with. A number of parameters can be used to control the resulting ultrathin film structure and thickness: concentration, ionic strength, dipping time, and so on. These films can also be prepared with a nearly unlimited range of functional groups incorporated within the structure of the film. Additionally, it has significant advantages over other techniques; for example, this process is independent of the substrate size and topology, the assembly is based on spontaneous adsorptions, and no stoichiometric control is necessary to maintain surface functionality. In the late 1990s, the layer-by-layer deposition of polyelectrolytes has been extended onto charged micrometer-sized particles. It has been shown that polyelectrolyte hollow capsules could thus be prepared by removing the core after the deposition to form "hollow-shell" particles. Since then, the technique has demonstrated an enormous variety of assembly mechanisms, using different substrate surfaces, shape of templates, and transformation in protocols, with the term layer-by-layer becoming synonymous with nanostructured materials and assembly of thin-film coatings, shell, and hollow-shell or tube formation. From the mechanistic side, other than simple electrostatic attraction of oppositely charged species, this technique now includes the use of other noncovalent interactions, for example, hydrogen bonding, stereocomplexation, dipole interactions, and so on. Covalent coupling protocols include click chemistry, thiol-ene-chemistry, and other chemical mechanisms. The list of species and objects that have been assembled includes a wide variety



Figure 1.1 Ultrathin organic molecular and macromolecular assembles including vapor-deposition methods based on monolayer and ultimately multilayer deposited systems.

of molecules, macromolecules, dendrimers, block-copolymer micelles, graphene, carbon nanotubes, nanoparticles, biological objects, and so on. For the substrates employed this has gone from simple glass slides and Si wafers to large-area substrates and nanoparticle surfaces. For the protocols employed, the list includes spin coating, spray assembly, large-area dipping, and roll-to-roll processes. A schematic diagram of these ultrathin molecular and macromolecular assembles including vapor deposition methods are shown in Figure 1.1. While the material of interest is mainly organic in nature, inorganic and organic–inorganic hybrid materials can be utilized in such protocols.

Of high interest in the past decade is the grafting of polymers by directly growing them from surface-tethered initiators otherwise known as surface-initiated polymerization or SIP to form polymer brushes (Figure 1.2). The "grafting-from" method is a departure from previous methods of grafting polymers by physical adsorption, for example, diblock-copolymer or amphiphilic polyelectrolytes including polymers with "anchoring groups." Other than physical adsorption, grafting by chemical adsorption of a preformed polymer, for example, one with an anchoring group at the end is also another route. This is almost an extension of 1 Deposition, Nanostructuring, Biological Function, and Surface Analytical Methods



Figure 1.2 Different methods of grafting polymers on surfaces based on methods of attachment of a preformed polymer or direct growth of the polymer from or through a surface based on specific polymerization mechanisms.

the SAM technique as applied to macromolecules and is sometimes referred to as a *"grafting-to"* approach. Another member of this class of polymer film formation is a *"grafting-through"* approach where the polymerization stitches through surface-tethered monomers. The reason the SIP has garnered so much popularity is that it has enabled the formation of polymers brushes with a high grafting density in which the polymer main chain is extended away from the surface. It has also enabled the polymerization in confined environments by well-known addition polymerization mechanisms including free-radical, anionic, cationic, metathesis, ring-opening, and living free-radical polymerization. The latter being the most reproducible and well controlled of all the polymerization processes so far reported.

Another aspect of thin polymer films concerns the more recent developments in the field of block-copolymer mesophase and nanophase structuring (Figure 1.3). While this aspect has been well studied in the bulk for the last three decades, new methods for templating, patterning, and applications take advantage of new polymer synthesis and microscopic and scattering characterization methods. The well-known phase separation between polymers of dissimilar χ -interaction parameters has taken on new meaning when applied to ultrathin films and in the presence of externally applied fields, for example, of static electric, magnetic, electromagnetic, and so on,. nature. It is of particular interest to introduce ternary compositions, for example, adding surfactants or nanoparticles and how this third



Figure 1.3 Different mesoscopic and nanoscopic structures based on phase separation induced by composition or field effects in thin films.

component affects the various traditionally reported mesophases of cylindrical, lamellar, or bicontinuous nature. On the mesoscopic scale one should emphasize the various aspects and methods for patterning. These include: photolithography, electron-beam lithography, soft lithography based on the popular microcontact printing technique, imprint lithography, and nanolithography in conjunction with surface probe microscopy.

It is well beyond the scope of this book to include here the most recent developments in plasma polymerization, physical and chemical vapor depositions, organic molecular beam epitaxy, hybrid materials layering, sol-gel and polymer coatings, electrodeposition, and electroplating. Even developments in traditional spin coating, roll-to-roll printing or a combination of the above techniques for new hybrid or multilayer films have been reported and are considered state-of-the-art.

There are many aspects of new materials that have been described in the literature that are based on new synthesis strategies or rely on the use of functional polymers. Other than the traditional polymers used in bulk and as thin-film coatings such as those based on vinyl polymers, methacrylates, urethanes, and polyesters, the most popular if not the ones with the highest potential for thin-film devices are in the area of electro-optical systems based on conducting or π -conjugated polymers. Conductive polymers can be accessed by electropolymerization or chemical oxidative methods. It is also possible to deposit preformed polymers that can be prepared by metal-mediated coupling reactions or by metathesis reactions. In this case there is a high interest in their crystallinity, orientation, charge carrier mobility, electrochromic properties, and so on. Perhaps in light of the recent Nobel Prize in Physics for 2010, graphene ultrathin films are expected to take center stage in terms of electro-optical applications.

Some of the most important developments in recent years refer to films for biological applications, made from building blocks of biological origin or are of a biomimetic nature. Simply speaking, one can use any of the above techniques and apply the resulting films for biological problems or conversely, looking for a materials solution by using well-known biological models. For example, by bringing together materials science and the biological world, it is possible to introduce tethering of the ubiquitous polyethylene glycol (PEG) for new biological architectures and interactions. PEG brushes can be made to be highly resistant to biofouling. Stimuli-responsive polymers with hydrogel structures including poly(N-isopropyl acryl amide) or PNIPAM polymers are equally important for drug release. Yet another development concerns architectures based on layer-by-layer systems or polymer brushes that can be used to control drug release or cell chemotaxis, ion gates, DNA capture, or to control cell proliferation on surfaces. Other examples are lipid bilayer membranes that can be artificially tethered to a solid surface using polymer-tethered lipids. An important aspect of biological systems as thin films is their applications in sensing (Figure 1.4), where it is important to enable specificity coupled with transduction. This concept allows for studies that enable quantification of phenomena normally observed only in in-vivo



Figure 1.4 Biomimetic systems can be coupled as thin-film materials on a variety of flat substrate surface connected with a transduction mechanism.

conditions and is a very good connection of new materials toward biophysics- and bioengineering-related projects.

The last but not the least aspect of organic polymer ultrathin films is developments related to surface analysis and characterization. A traditional division is the use of optical/spectroscopic, microscopic, and scattering methods. However, one should add other techniques like piezoelectric (acoustic) or electrochemical (including impedance) into this menu. Traditional optical/spectroscopic methods include transmission, absorption, and fluorescence spectroscopies. New variations include single molecule fluorescence and fluorescence photocorrelation spectroscopies. Microscopy techniques include optical, surface probe microscopies (SPMs), as well as electron microscopies including transmission electron microscopy (TEM) and scanning electron microscopy (SEM). SPM methods, which includes atomic force microscopy (AFM) and scanning tunneling microscopy (STM), have truly been of wide utility to complement the TEM and SEM methods. Scattering methods include X-ray and neutron diffraction, scattering, reflectometry, and so on. There are many techniques that are very specific to the geometry of the measurement. Optical methods deserve their own classification since they can include many hyphenated techniques and functions dealing with spectroscopy and microscopy. Well-known methods include waveguides, ellipsometry, interferometry, surface plasmon resonance, dielectric spectroscopy, Raman scattering, and so on Surface plasmon resonance (SPR) spectroscopy together with optical waveguiding spectroscopy (OWS) in particular, has been a method of choice not only for optical and dielectric measurements but also for their versatility toward hyphenated techniques-a recent combination with AFM and electrochemistry is an example (Figure 1.5). This has enabled applications in materials science and in the investigation of biophysical





real-time detection of optical and electrochemical phenomena coupled with morphology investigation in films – including electropolymerization of conducting polymers.

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phenomena based on coupling the films of interest on a gold- or silver-coated glass/prism surface. The open environment on one side means that the experiment can be done *in situ* or in real time with simultaneous parameters monitored as a function of reflectivity, angle, time, and wavelength. Applications with microscopy and fluorescence further extend its utility as a characterization tool or for sensing.

In the area of electrochemical analysis, it is possible to use this to probe electron transfer and redox properties of polymer species. In impedance analysis it is possible to use model circuits to explain the behavior of ion and/or charge transport and film structure although for certain systems it is not always easy to derive a generally accepted model. Acoustic methods such as the quartz crystal microbalance (QCM) and surface acoustic waves (SAWs) methods are useful for probing not only the deposition of mass but also the mechanical properties of thin films. There are many more unconventional techniques that can be mentioned. These include, the surface force apparatus (SFA), streaming potential measurements, Kelvin probe methods, photobleaching experiments, and so on.

This chapter has covered-in a very comprehensive but succinct way-our perspective of what constitutes the field of organic and polymer thin films.