Multilayer Thin Films

Sequential Assembly of Nanocomposite Materials

Edited by
Gero Decher, Joseph B. Schlenoff

WILEY-VCH

Multilayer Thin Films

Sequential Assembly of Nanocomposite Materials

Edited by G. Decher, J. B. Schlenoff

Multilayer Thin Films

Sequential Assembly of Nanocomposite Materials

Edited by
Gero Decher, Joseph B. Schlenoff

WILEY-VCH

Gero Decher
Institut Charles Sadron
6, rue Boussingault
F-67083 Strasbourg Cedex
France

Joseph B. Schlenoff
Florida State University
Dept. of Chemistry and Biochemistry
Tallahassee, Florida 32306-4390
USA

Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library.

Bibliographic information published by Die Deutsche Bibliothek
Die Deutsche Bibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data is available in the Internet at http://dnb.ddb.de

Printed in the Federal Republic of Germany
Printed on acid-free paper

Typesetting K+V Fotosatz GmbH, Beerfelden
Printing Strauss Offsetdruck GmbH, Mörlenbach
Bookbinding J. Schäffer GmbH & Co. KG, Grünstadt

ISBN 3-527-30440-1

Foreword

Over the last ten years, scientists from varying backgrounds have rallied around a versatile new method for the synthesis of thin films. Because the layer-by-layer assembly method provides opportunities for creative design and application of function-specific films, the field has experienced an initial period of exponential growth. This book, the first on the topic, contains many insightful contributions from leaders in the field that will enable novices and experts to understand the promises and premises of multilayers.

Readers will instantly identify with a particular aspect of the technology, whether it is the design and synthesis of new polymeric or nanoparticulate building blocks, understanding the polymer physical chemistry of multilayers, or characterizing their optical, electrical or biological activities. The reasons for the intense interest in the field are also clearly evident: multilayers bridge the gap between monolayers and spun-on or dip-coated films, and they provide many of the aspects of control found in classical Langmuir-Blodget (LB) films, yet multilayers are more versatile, in many respects, and easier to create.

This book is an essential and welcome addition to the literature on thin films. Readers with interests in self-assembled systems, supramolecular chemistry, nanocomposites or polymers will find themselves fascinated by the diversity of topics herein. The message that multilayers are making significant inroads into numerous aspects of chemistry, physics and biology is made clear. The editors and authors are to be commended for creating a comprehensive yet readable volume.

Jean-Marie Lehn

Contents

Preface

When a new field is growing exponentially, as judged by the number of publications, presentations and patents, when is the "right" time to assemble a volume of contributed chapters from some of the acknowledged leaders in the field? What if every potential contributor is incredibly busy, following up an ever-expanding plethora of ideas and experiments? It was in this harried atmosphere that our colleagues carved out the time to write their contributions. We are extremely grateful to them for gathering their thoughts and accomplishments into chapters.

The idea for this book came together following a very successful symposium at the ACS in San Francisco 2000, which we organized. No volume on the topic had yet been published, but there was already a large store of knowledge that had been created as groups had responded enthusiastically to the promise of the first few papers appearing in the early 90's. Multilayers had gathered a great deal of momentum, flourishing in the more "informal" space of papers, preprints, talks and word-of-mouth. By 2000, the field had simply outgrown informality.

We had been riding the wave of this activity, enjoying a growing number of colleagues. We were fully aware of the infectious nature of multilayers research, which is like a good mystery novel – hard to put down once you start. We are honored to have been in the thick of things during the early years. Every experiment was significant and the results suggested several more experiments. This dizzying atmosphere pervades even today: ask any multilayerer!

We are pleased to have edited this book. Our object was not only to document what is known about multilayers, but also to promote the potential of these versatile thin films and to facilitate the adoption of the technology by others. The field is new. We are proud of its ability to catalyze interdisciplinary thought and action. In this regard, multilayers represent a model platform for promoting modern research. Also, the intellectual distance between concept and application is minimal. Commercial applications have already been realized.

We hope the message of abundant research opportunities is made loud and clear. It is easy to get started. Easy to get "hooked." This book is essential in showing you how. We look forward to more elegant and complex multilayered architectures and functionalities, as well as significant expansion at the biological/biomedical interface.

Finally, we would like to express our thanks to Jean-Marie Lehn for his support in writing the forword. His "big-picture" viewpoint is sincerely appreciated.

August 2002

Gero Decher
Joe Schlenoff

List of Contributors

M. L. Bruening
Department of Chemistry
Michigan State University
East Lansing, MI 48824
bruening@cem.msu.edu
USA

F. Caruso,
Max Planck Institute of Colloids and Interfaces
D-14424 Potsdam
caruso@servg.mpikg-golm.mpg.de
Germany

M. Castelnovo
Institut Charles Sadron
6, rue Boussingault
F-67083 Strasbourg Cedex
France

R. O. Claus,
Fiber & Electro-Optics Research Center
Virginia Tech
106 Plantation Road
Blacksburg, VA 24061-0356
roclaus@vatech.edu
USA

K. L. Cooper
NanoSonic Inc.
1485 South Main Street
Blacksburg, VA 24060
USA

G. Decher
Institut Charles Sadron
6, rue Boussingault
F-67083 Strasbourg Cedex
decher@cerbere.u-strasbg.fr
France

E. Donath,
Max Planck Institute of Colloids and Interfaces
D-14424 Potsdam
edwin.donath@mpikg-golm.mpg.de
Germany

J. H. Fendler
Center for Advanced Materials Processing
Clarkson University
Potsdam, NY 13699-5814
fendler@clarkson.edu
USA

K. Glinel,
Unite de Physique et de Chimie des hauts polymères (POLY)
Université Catholique de Louvain
Place Croix du Sud, 1
B-1348 Louvain-la-Neuve
glinel@poly.ucl.ac.be
Belgium

P. T. Hammond
Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139
hammond@mit.edu
USA

I. Ichinose,
Topochemical Design Laboratory
Frontier Research System
Institute of Physical
and Chemical Research (RIKEN)
2-1 Hirosawa, Wako
Saitama
351-0198 Japan
izumi@postman.riken.go.jp

J. F. Joanny
Physicochimie Curie
Institut Curie Section Recherche
26, Rue d'Ulm
F-75248 Paris Cedex 05
joanny@ics.u-strasbg.fr
France

A. Jonas
Unite de Physique et de Chimie
des hauts polymères (POLY)
Université Catholique de Louvain
Place Croix du Sud, 1
B-1348 Louvain-la-Neuve
jonas@poly.ucl.ac.be
Belgium

V. Kabanov
Chemistry Department
Moscow State University
119899 Moscow
kabanov@libro.genebee.msu.su
Russia

R. Klitzing
Iwan-N.-Stranski-Institut (Sekr. ER 1)
TU Berlin
Straße des 17. Juni 112
D-10623 Berlin
klitzing@chem.zu-berlin.de
Germany

N. A. Kotov
Department of Chemistry
Oklahoma State University
Stillwater, OK 74078
kotov@okstate.edu
USA

T. Kunitake
Topochemical Design Laboratory
Frontier Research System
Institute of Physical
and Chemical Research (RIKEN)
2-1 Hirosawa, Wako
Saitama
351-0198 Japan
kunitake@ruby.ocn.ne.jp

K. Kuroiwa
Department of Chemistry
and Biochemistry
Graduate School of Engineering
Kyushu University
Japan

D. Kurth,
Max Planck Institute of Colloids and
Interfaces
D-14424 Potsdam
kurth@.mpikg-golm.mpg.de
Germany

A. Laschewsky,
Fraunhofer Institute
Geiselbergstraße 69
14476 Golm
andre.laschewsky@iap.fraunhofer.de
Germany

Y. Lvov
Institute for Micromanufacturing and
Chemistry Department
Lousiana Tech University
P.O. Box 10137
Ruston, LA 71272
ylvov@coes.latech.edu
USA

H. Möhwald,
Max Planck Institute of Colloids and Interfaces
D-14424 Potsdam
moehwald@mpikg-golm.mpg.de
Germany

H. Riegler,
Max Planck Institute of Colloids and Interfaces
D-14424 Potsdam
hans.riegler@.mpikg-golm.mpg.de
Germany

M. F. Rubner
Department of Materials Science and Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139
rubner@mit.edu
USA

J. Schlenoff
Chemistry Department
Florida State University
Tallahassee, FL 32306-4390
schlen@chem.fsu.edu
USA

J. Shen,
Key Laboratory for Supramolecular Structure and Spectroscopy,
Department of Chemistry,
Jilin University
Changchun
130023 People's Republic of China
sjc@mail.jlu.edu.cn

G. Sukhorukov
Max Planck Institute of Colloids and Interfaces
D-14424 Potsdam
Germany

B. Tieke
Institut für Physikalische Chemie
Universität zu Köln
Luxemburger Straße 116
D-50939 Köln
tieke@uni-koeln.de
Germany

P. Y. Vuillaume
Unite de Chimie des materiaux (CMAT)
Université Catholique de Louvain
Place Louis Pasteur 1
B-1348 Louvain-la-Neuve
vuillaume@chim.ucl.ac.be
Belgium

Y.-X. Wang,
Fiber & Electro-Optics Research Center
Virginia Tech
106 Plantation Road
Blacksburg, VA 24061-0356
USA

L. Zhang,
Fiber & Electro-Optics Research Center
Virginia Tech
106 Plantation Road
Blacksburg, VA 24061-0356
USA

X. Zhang
Key Laboratory for Supramolecular Structure and Spectroscopy,
Department of Chemistry,
Jilin University
Changchun
130023 People's Republic of China
xi@mail.jlu.edu.cn

1
Polyelectrolyte Multilayers, an Overview

G. Decher

1.1
Why is the Nanoscale so Interesting?

In our research team, we strongly believe that the functionality of any object (on any length scale) arises from the intricate interplay of its constituents. In complex systems, new properties appear that are not observed for each individual component. While it is trivial that electrons and nuclei form atoms (sub-ångstrom scale), that atoms form molecules (ångstrom scale) or that monomers can be transformed into polymers (early nanometer scale), we are just beginning to explore the potential of supramolecular assemblies or of large multifunctional objects (e.g. copolymers of complex architecture). While nature plays with the full range of objects on the length scale from femtometers to parsecs, mankind is somewhat limited to the length scale between subatomic particles and the size of our planet. Although the range accessible to man is already reduced, we hardly master more than a fraction of what is available to us. A particularly interesting length scale is, of course, the nanoscopic organization of matter. Taking life as the most fascinating and complex property of matter, nature clearly shows that the minimum size of a lifeform (in the definition of life as we know it) is of nanoscopic to microscopic dimension. It is exactly this length scale that is just being touched but not mastered by either bottom up (chemical synthesis) or top down (miniaturization) approaches. Fig. 1.1 summarizes our philosophy and motivation for working on the synthesis, properties and fabrication of complex nanoorganized and nanocomposite materials.

1.2
From Self-Assembly to Directed Assembly

Suppose you do not like the way materials end up being arranged after carrying out a self-assembly experiment and obtaining equilibrium. The obvious pathway for improvements seems to be to re-engineer the chemical structure of the molecules involved and to hope to obtain a more suitable structure with the new molecules. This is often time-consuming as several optimization cycles are frequently required.

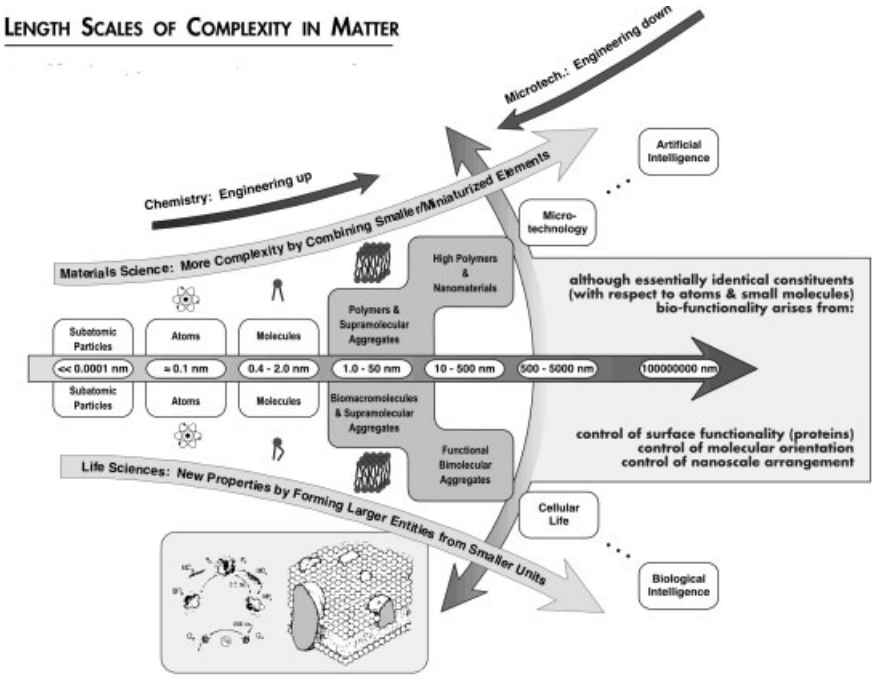

Fig. 1.1 Complexity as a function of length scale. Materials Science is not yet as far advanced as the evolutionary developments present everywhere in nature. The photosystem is just one example of the precise spatial assembly of a functional molecular machine. The drawing is adapted from [1].

Another possible route to a desired target structure is to use an assembly procedure that prevents equilibrium by trapping every compound kinetically in a predetermined spatial arrangement. At present there are only very few approaches in this direction. Most of the work has been carried out for the simplest case, in which different materials are put in one-dimensional order in a multilayer film. For about 65 years the molecularly controlled fabrication of nanostructured films has been dominated by the conceptually elegant Langmuir-Blodgett (LB) technique, in which monolayers are formed on a water surface and subsequently transferred onto a solid support [2, 3]. The pioneering work on synthetic nanoscale multicomposites of organic molecules was carried out by Kuhn and colleagues in the late 1960s using the LB technique [4]. His experiments with donor and acceptor dyes in different layers of LB films provided direct proof of distance-dependent Förster energy transfer on the nanoscale. These were also the first true nanomanipulations as they allowed for mechanical handling of individual molecular layers such as separation and contact formation with ångstrom precision [5]. Unfortunately the LB technique is rather limited with respect to the set of molecular components suitable for LB deposition, and molecules are often not firmly trapped and frequently rearrange after or even during deposition.

1.3
The Layer-by-Layer Deposition Technique

The so-called layer-by-layer (LbL) deposition technique [6–14] (Fig. 1.2) also falls into the category of template assisted assembly. Template assisted assembly is much faster than self-assembly/chemical modification cycles whose outcome is often uncertain or difficult to predict. For the case of LbL-deposition, it can be tailored to even allow multimaterial assembly of several compounds without special chemical modifications [15–19], thus giving access to multilayer films whose complex functionality can fall into the two following categories:

1. Tailoring of surface interactions: Every object interacts with its environment via its surface. Thus all properties depending on this interaction are dictated by surface functionality which can be tailored for many needs (e.g. corrosion protection [20], antireflective coatings [21], antistatic coatings, stickiness or non-stickiness [22], surface induced nucleation [23–26], antifouling [27–29], hydrophilicity or hydrophobicity, biocompatibility [30, 31], antibacterial properties, molecular recognition, chemical sensing or biosensing [32–46], microchannel flow control [47, 48]…).

2. Fabrication of surface based devices: The sequence of deposition of different materials defines the multilayer architecture and thus the device properties. One may call this knowledge based (or programmed, or directed, or controlled, or template assisted) assembly, in contrast to self-assembly. It leads to property engineering by controlling the mostly one-dimensional spatial arrangement of functionality in multimaterial layered nanocomposites (membrane reactors [49–51], photonic devices such as light emitting diodes [52–75] or complex waveguides, compartmentalized films with barrier layers or separation membranes [34, 44, 75–83],…).

The fabrication of multicomposite films by the LbL procedure means literally the nanoscopic assembly of hundreds of different materials in a single device using environmentally friendly, ultra-low-cost techniques. The materials can be small organic molecules or inorganic compounds [7, 61, 84–99], macromolecules [12, 39, 53, 55, 76, 86, 100–116, 117–125], biomacromolecules such as proteins or DNA [15–18, 30, 32, 49, 50, 126–151] or even colloids (metallic or oxidic colloids or latex particles) [18, 21, 75, 79, 98, 108, 121, 142, 152–198]. The technique can be applied to solvent accessible surfaces of almost any kind and any shape, the more exotic ones being microcapsules, colloids or biological cells [104, 122, 199–206].

Note that the list of references above is intended to give some introductory information on some recent developments of layer-by-layer assembly. Since many groups have provided reviews of their excellent work for this book, a complete reference list to all of their work is not needed in this overview chapter. A more detailed history of LbL deposition, the principle of which was apparently first described by Iler [207], is found in a recent review [208]. In the last eight years the field has been reviewed on several occasions outlining the concepts behind and the potential of the LbL technology [208–215]. The approach has spread from our laboratory to the international community and kindled research of physicists, che-

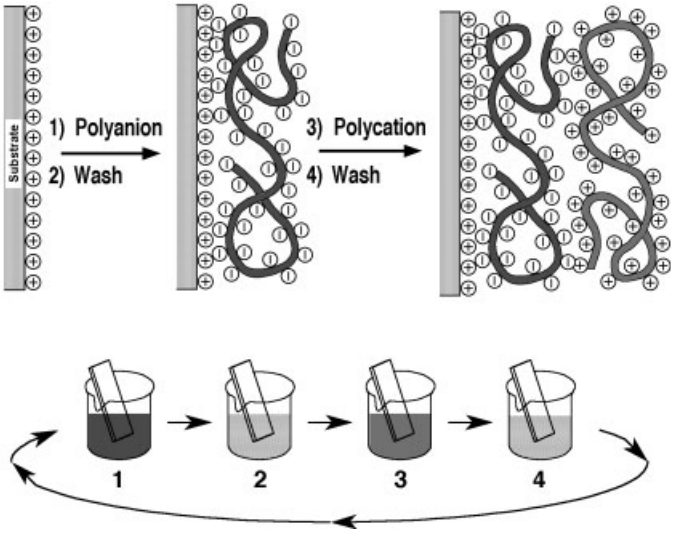

Fig. 1.2 Top: Simplified molecular concept of the first two adsorption steps depicting film deposition starting with a positively charged substrate. The polyion conformation and layer interpenetration are an idealization of the surface charge reversal with each adsorption step which is the basis of the electrostatically driven multilayer buildup depicted here. Counterions are omitted for clarity. Bottom: Schematic of the film deposition process using glass slides and beakers. Steps 1 and 3 represent the adsorption of a polyanion and polycation respectively, and steps 2 and 4 are washing steps. The four steps are the basic buildup sequence for the simplest film architecture $(A/B)_n$ where n is the number of deposition cycles. The construction of more complex film architectures requires additional beakers and an extended deposition sequence.

mists and of scientists in the biomedical field, because it is extremely powerful yet simple to use and because it challenges theory at the level of polyelectrolyte adsorption.

1.3.1
LbL Deposition is the Synthesis of Polydisperse Supramolecular Objects

For most cases an LbL film has a unique layer sequence that depends strictly on the deposition sequence. This points to the fact that LbL deposition should be considered as an analogue to a chemical reaction sequence (Fig. 1.3). While a chemical reaction takes place between different synthons and typically yields a unique molecule after each synthetic step, layer-by-layer deposition involves the adsorption of a single species in each adsorption step and yields a multilayer film with a defined layer sequence. While molecules are synthesized in several consecutive reaction steps, a multicomposite film is fabricated in several adsorption steps.

The reagents in classic synthesis are typically molecules, in layer-by-layer deposition they can be chosen from a wide range of materials. This is represented schematically in Fig. 1.4. While today most of the multilayer films have been fabri-

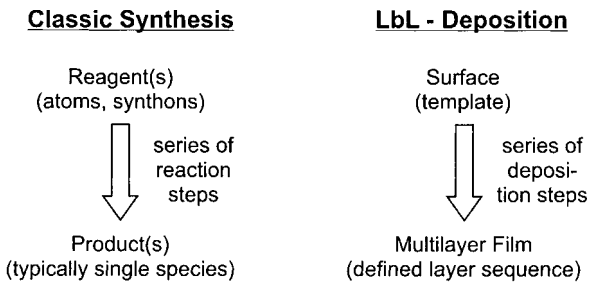

Fig. 1.3 Analogy of chemical multistep synthesis and multilayer deposition, both leading to a unique molecular and supramolecular species (multilayer film).

cated using mainly electrostatic attraction as the driving force for multilayer build-up, this is by no means a prerequisite. There are many other interactions that have been used successfully for multilayer deposition including: donor/acceptor interactions [216-218], hydrogen bonding [173, 219–224], adsorption/drying cycles [225, 226], covalent bonds [11, 14, 45, 227–238], stereocomplex formation [239–241] or specific recognition [6, 17, 126, 128, 132, 139, 242–246].

In general one needs just any interaction (this may be one or several different interactions) between two species "reagents" in order to incorporate them into a multilayer film. The interaction can easily be tested in solution prior to carrying out the deposition if both film constituents are soluble in the same solvent. When

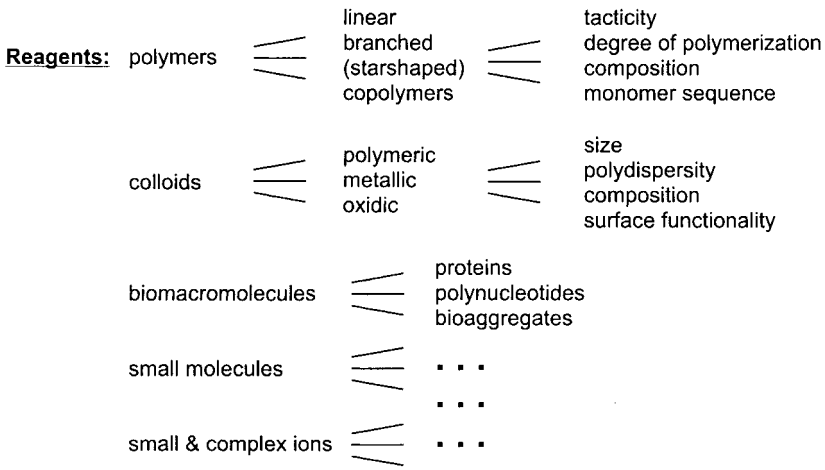

Fig. 1.4 Reagents for layer-by-layer deposition. Some details on composition and structural properties are shown for polymers and colloids. To keep the schematic simple, this level of detail is not carried through for the last three types of reagents. One should also note that small molecules and complex ions are sometimes more difficult to incorporate into multilayer films in a regular way than, for example, charged macromolecules.

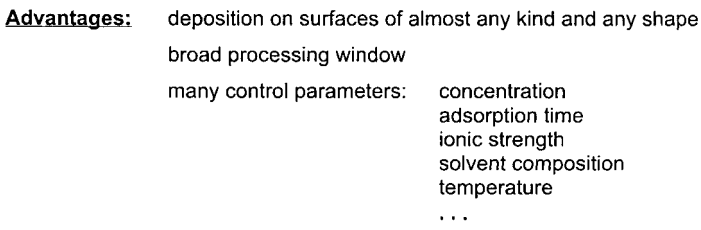

Fig. 1.5 Summary of some of the advantages of layer-by-layer deposition. While the structure and properties of each layer depend on certain control parameters as mentioned above, the deposition is highly reproducible if these parameters are maintained strictly constant.

both solutions are mixed and flocculation occurs it is a good sign that multilayer fabrication will be possible. This is only a very crude test: multilayer formation may also be possible in the absence of flocculation.

Given the large set of materials which are easily incorporated into multilayer films, layer-by-layer deposition is a rather general approach for the fabrication of complex surface coatings. It combines several advantages as shown in Fig. 1.5. It is possible to coat almost any solvent-accessible surface starting with sub-micron objects [104, 122, 199-202, 204–206] up to the inside of tubings or even objects with a surface of several square meters. Like a chemical reaction, the precise structure of each layer depends on a set of control parameters such as concentration, adsorption times, ionic strength (e.g. [9]), pH (e.g. [247]), or temperature (e.g. [248]), but in general the processing window is rather broad.

1.3.2 Reproducibility and Deposition Conditions

The question of reproducibility arises immediately when we draw the analogy between a chemical reaction and layer-by-layer adsorption. At first sight one may say that molecules are unique species and multilayer films are "only" ill-defined supramolecular objects. This is essentially the same argument that has downgraded macromolecular chemistry for years in comparison to organic chemistry. Today it is generally accepted that "ill-defined" macromolecules are also unique species that can indeed be well described by distributions and average properties like polydispersity or degree of polymerisation. The situation is similar for multilayer films as they are characterised by a sequence of layers in which each layer has its individual structure and properties. While the sequence of layers is as strict as the arrangement of atoms in a molecule, the properties of each layer can only be described as an average over a certain area. The most obvious property of an individual layer is its thickness, which is dependent on the nature of the underlying surface and on the deposition conditions. Parameters presumed to be important with respect to the underlying surface are, for example, the nature and density of charged groups, their local mobility (in the case of a polymeric surface) and the

surface roughness. The most important reaction parameters or deposition conditions are mentioned in Fig. 1.5. However, the list is somewhat longer including: solvent, concentration of adsorbing species, adsorption time, temperature, nature and concentration of added salt, rinsing time, humidity of the surrounding air, drying, agitation during adsorption or rinsing, dipping speed and so forth. While the LbL technique generally works very well due to the fact that the processing window is rather large, it is highly recommended to keep the deposition conditions as constant as possible in order to get highly reproducible results. If this is done rigorously, one obtains films composed of tens of layers whose thickness for example, differs by about one percent. When comparing data, one should not overlook that it is not sufficient only to maintain the deposition conditions exactly, but also the conditions under which the measurements were taken. Fig. 1.6 shows an example of how the film thickness of a $(PSS/PAH)_8$ multilayer film, for which both polyions were deposited from solutions containing 2 M sodium chloride, depends on the temperature and on the relative humidity at the time of the measurement.

Often it is said that polyelectrolyte multilayer films are independent of the underlying substrate. This is an oversimplified statement, of course there is a dependence on the underlying surface as stated above. However, since polyanion and polycation adsorption is repeated consecutively, each polyanion adsorbs onto a polycation-covered surface and vice versa. This means that, after a few layers, the structure and properties of each layer are governed by the choice of polyanion/polycation pair and by the deposition conditions and that the influence of the substrate is typically lost after a few deposition cycles. The issue of the substrate is examined again when discussing soft and rigid materials later.

1.3.3 Monitoring Multilayer Buildup

1.3.3.1 Ex-situ Characterisation

The easiest way to follow multilayer buildup is probably by UV/Vis spectroscopy, which works for all colored materials. Fig. 1.7 is an example for poly(styrene sulfonate)/poly(allyl amine) (PSS/PAH) films which constitute probably the best characterised system at present.

Equivalent to measuring the optical absorbance, one can also determine the film thickness by ellipsometry or X-ray reflectometry as shown in Fig. 1.8. The reflectivity traces on the left were taken on a dry specimen at various stages of multilayer buildup. Each trace corresponds to a single data point in the diagram on the right. In this case PSS was deposited from aqueous solutions containing different amounts of salt, while PAH was deposited from pure water. One clearly sees that the film thickness is slightly, but very precisely, increased with increasing salt concentrations [9]. This effect would be much stronger if both polyions were deposited from solutions containing salt. The fact that only interference fringes resulting from the total film thickness are observed in such samples will be discussed in the section on the structure of multilayer films. The salt concen-

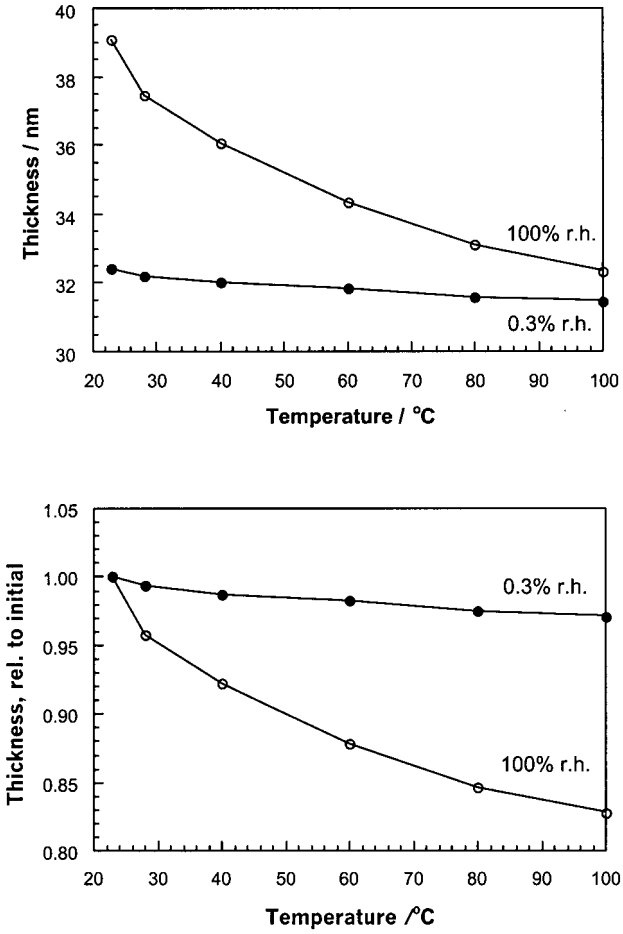

Fig. 1.6 Top: Film thickness of the same multilayer specimen as a function of temperature and of relative humidity (r.h.). The differences in thickness at identical temperatures are entirely due to a difference in water content within the film and not due to a negative thermal expansion coefficient. This difference becomes less pronounced at elevated temperature, when the water is driven out of the film. Bottom: The same data as above, but normalised with respect to the initial film thickness. It becomes obvious that even small differences in temperature or humidity can easily account for changes in film thickness of the order of 5–10% depending on the swellability of the film. (G. Sukhorukov, J. Schmitt and G. Decher, unpublished results.)

tration is not the only parameter that allows one to control the thickness of individual layers. Rubner has shown that, for the case of weak polyelectrolytes, layer thickness can be precisely controlled by pH [247].

While the two methods above are simple but sufficient to get some preliminary ideas on the deposition behaviour, there are numerous additional characterization methods described in the other chapters of this book. Very recently, nuclear mag-