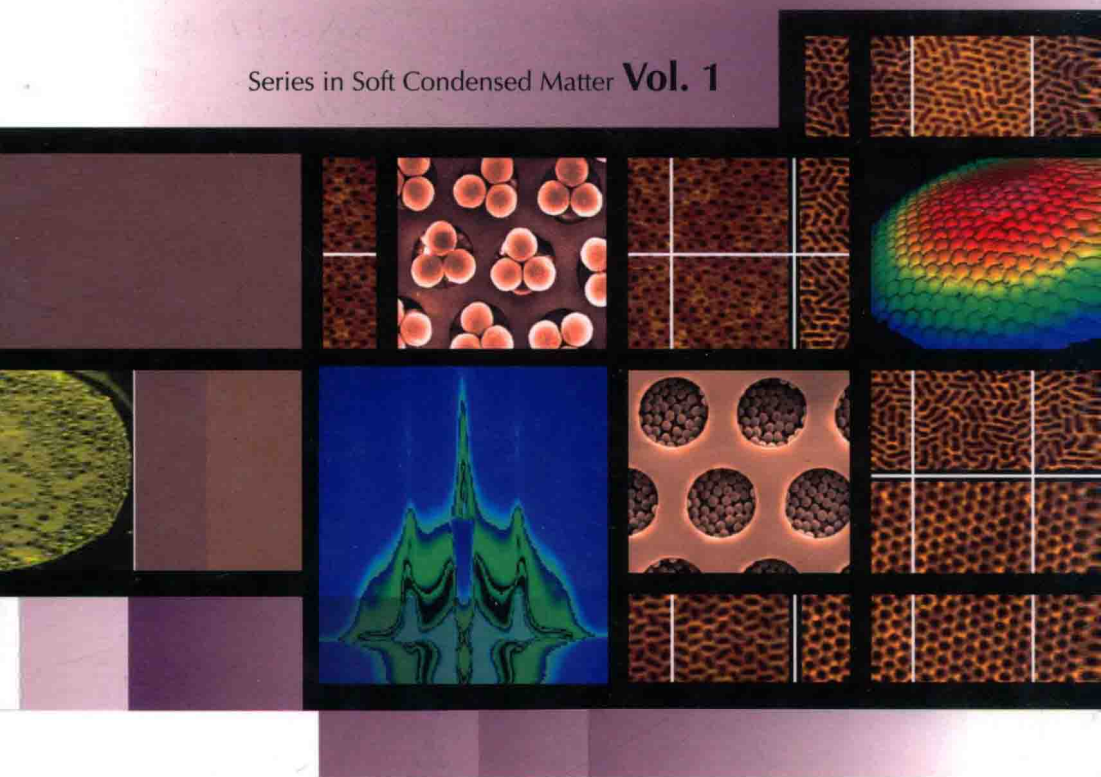


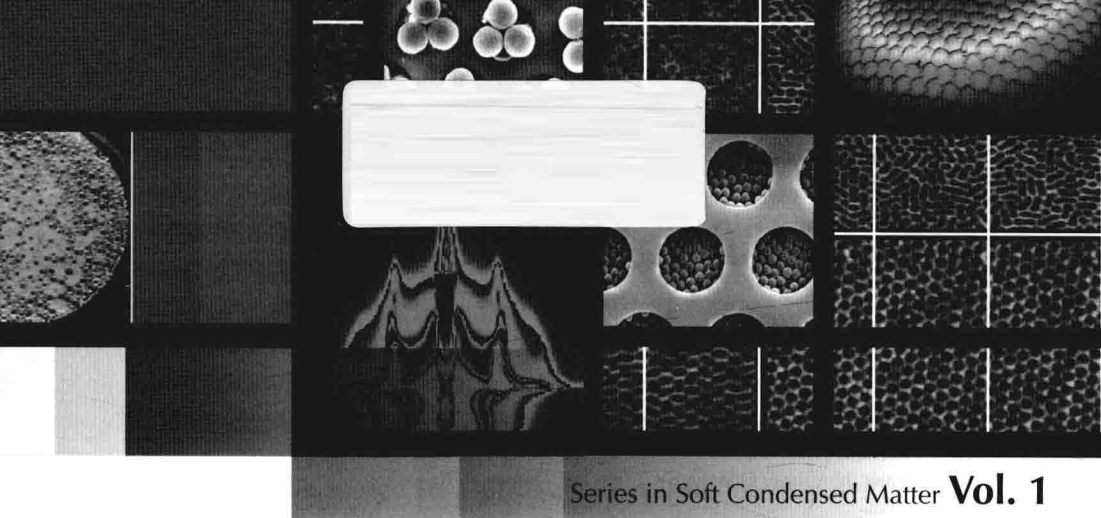
Series in Soft Condensed Matter **Vol. 1**



Editors

Ophelia K. C. Tsui • Thomas P. Russell

POLYMER THIN FILMS



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POLYMER THIN FILMS

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Aims & Scope

The study of *Soft Condensed Matter* has stimulated fruitful interactions between physicists, chemists, and engineers, and is now reaching out to biologists. A broad interdisciplinary community involving all these areas of science has emerged over the last 30 years, and with it our knowledge of *Soft Condensed Matter* has grown considerably with the active investigations of polymers, supramolecular assemblies of designed organic molecules, liquid crystals, colloids, lyotropic systems, emulsions, biopolymers, and biomembranes, among others.

The present Book Series, initiated by Pierre-Gilles de Gennes, covers a large number of diverse aspects, both theoretical and experimental, in all areas of *Soft Condensed Matter*. It mainly addresses graduate students and junior researchers as an introduction to new fields, but it should also be useful to experienced people considering a change in their field of research. This Book Series aims to provide a comprehensive and instructive overview of all *Soft Condensed Matter* phenomena.

Published:

Vol. 1 Polymer Thin Films

edited by Ophelia K. C. Tsui and Thomas P. Russell

PREFACE

Everyday we are exposed to a myriad of applications of polymer thin films. This is whether it occurs in food wrapping, the packaging of virtually any item that is sold, or in protective coatings placed on the surface of furniture or glass. More and more often, though, the thickness of the polymer film decreases to dimensions comparable to the dimensions of a single polymer chain, or in the case of block copolymers or mixtures, comparable to the characteristic period of the microphase separated or phase separated morphology. For example, in the case of microelectronic circuits where polymers can be used as a dielectric insulator or as a template to produce a porous oxide layer, the dimensions of and separation distance between the conducting elements is rapidly decreasing to several tens of nanometers. We are forced, therefore, to ask the question as to whether the confinement of the polymer to such small dimensions will change the fundamental characteristics of the polymer. In addition, with such small scale features, the surface to volume ratio increases significantly, so does the abundance of interfacial area affect the nature of the polymer in the confined geometry. In the case of block copolymers, how does such confinement alter the nature or orientation of the microphase-separated morphology? More importantly, if we can understand the influence of such confinement, can we use this to our advantage in designing systems to induce behavior not seen in the bulk or can we control the interactions of the polymer or block copolymer with the interfaces to manipulate the spatial arrangement of the nanoscopic elements in the morphology? If so, then this will open numerous applications of polymers and block copolymers in the burgeoning field of nanotechnology which encompasses applications ranging from ultrahigh density storage media, ultralow dielectric constant materials, high resolution separations media,

self-healing and self-corralling nanocomposites, flexible electronics and displays, and photovoltaic devices. Consequently, there has been a significant growth in the amount of research dedicated to understanding the structure and properties of polymer thin films.

The growth in the interest of polymer thin films has also been catalyzed by the increase in the number of techniques available to characterize thin polymer films. While these techniques may have been available for decades, only recently has it been recognized that they could be used to great advantage to characterize polymeric materials. Some of these techniques include scanning probe microscopies, neutron and x-ray reflectivity, grazing incidence x-ray scattering, forward recoil and Rutherford backscattering spectroscopies, dynamic secondary ion mass spectroscopy, x-ray microscopy and electron tomography. The growth in the use of these techniques to characterize polymer thin films, coupled with the use of fairly standard techniques, like ellipsometry, x-ray photoelectron spectroscopy, electron microscopy, x-ray and neutron scattering, dielectric spectroscopy, infrared and Raman spectroscopies, and optical microscopy, has revolutionized our understanding of polymer thin films. At the same time, there have been tremendous advances made in modifying either the chemical nature or the topography of surfaces, by use of photolithography, electron beam lithography, ion beam etching, and surface specific chemistries. This has imparted elegant routes to control the interactions between a polymer and a surface.

Perhaps the most significant development in the characterization of polymer thin films is the interest that a broad scientific community has taken in this area. From the engineering side, there are challenges that are faced in producing perfectly uniform thin films. Yet, this in turn has sparked the interest from the physics community in studies on instabilities in thin films and on the confinement of highly ordered structures. Controlling interfacial interactions has presented numerous challenges to surface chemists, both small molecule chemists and polymer chemists. The influence of confinement on phase transitions like crystallization, phase separation and microphase separation, has piqued the interest of physicists and physical chemists. Producing surfaces with well-defined topographies, chemistries and mechanical properties

has enabled the manipulation of the interactions of living cells with surfaces, and as such, has generated interest from the biological and microbiological communities. This convergence of interest from a wide-range of different disciplines has further promoted advances in our understanding of thin polymer films.

An overview encompassing the large variety of areas that have spun off from this vastly developing field is overdue. It is, however, important that this overview be understandable by the novice to the area and appreciated by the experts. This is the rather daunting task that faced the authors of the different chapters in this book. We hope that these chapters will serve as a useful resource for instructors of undergraduate and graduate courses. To reflect the interdisciplinarity, the authors of the different chapters include chemists, engineers, materials scientists and physicists that have made significant contributions in their respective areas.

This book contains eleven chapters that can be categorized into six major areas:

- The design and construction of nanostructures in block copolymer films — the fundamental principles, fabrication methods and applications (Ch. 1–4)
- Alternative methods of fabricating sophisticated nanostructures in polymer thin films (Ch. 5–6)
- Crystallization of polymers confined in nanometer films (Ch. 7)
- Tribology of polymer thin films — friction and adhesion (Ch. 8 and 9, respectively)
- Wetting stability of polymer films supported by a substrate (Ch. 10)
- Novel dynamical properties of polymer nanometer films (Ch. 11)

We are indebted to the contributors of this book who have abided to the cause and taken time and effort in completing the chapters. Despite the crash of a hard disk (Shimomura), laboratory floods (Jacobs) and over-commitment of time (all of the authors), the chapters were completed in a timely manner, are of high-quality, and a pleasure to read. We are grateful to the students and postdoctoral fellows in our groups (Z. Yang, J. Wang, R. Tangirala, W. Chen, J. Xu, J. Chen, D. Chen, L. Li,

P. Dobriyal, J. He and H. Liu) who had helped compile the subject index. Special thanks are due to the anonymous reviewers who had generously contributed their time in reading the chapters and given suggestions for improvements.

We hope that the students, professors and researchers will find this book a useful guide and resource to the field of polymer thin films.

O. K. C. Tsui

T. P. Russell

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CHAPTER 1

BLOCK COPOLYMER THIN FILMS

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The behavior of amorphous block copolymers (BCPs) in thin films depends on a combination of segmental interactions, interfacial interactions, surface energies and entropy. Commensurability between the film thickness, h , and the natural period, L_0 , of the microdomains in the bulk is also of importance. This chapter summarizes recent developments in our understanding of the influence of confinement, surface energies and surface heterogeneities on the morphology of BCP thin films, the use of thin BCP films as scaffolds and templates for the fabrication of nanostructured materials, and the generation BCP arrays in thin films having long-range lateral order for potential addressable media.

1. Introduction

Block copolymers (BCPs) consist of two or more chemically different polymer chains joined covalently at their ends. Due to the positive enthalpy and small entropy of mixing, dissimilar blocks tend to microphase separate into well-ordered arrays of domains, classically termed microdomains. The sizes of these microdomains, due to the connectivity of the blocks, are limited to molecular dimensions and, as such, are tens of nanometers or less. At temperature below an order-to-disorder transition temperature, T_{ODT} , BCPs microphase separate into

arrays of spherical, cylindrical, gyroid or lamellar microdomains, depending on the volume fractions of the blocks, f , and the degree of microphase separation, χN , where χ is the Flory-Huggins segmental interaction parameter and N is the total number of segments in BCPs. Above the T_{ODT} , BCPs phase mix and are disordered.

The self-assembly of BCPs into well-defined morphologies has opened numerous applications ranging from drug delivery to structural materials. In contrast to the bulk, the morphology of amorphous BCP thin films can be strongly influenced by surface and interfacial energies as well as the commensurability between the film thickness, h , and the period of the microdomain morphology, L_0 . With decreasing film thickness these parameters become increasingly important in defining the morphology. By controlling the orientation and lateral ordering the BCP microdomains in thin films, unique opportunities in the use of BCPs in materials science (adhesive properties, lubrication, membranes, and coatings), lithography and microfabrication (addressable memory, magnetic storage, insulating foams) and device technologies (light-emitting diodes, photodiodes, and transistors) are beginning to emerge. In this chapter, two aspects of BCP thin films will be addressed. First, the effect of confinement, surface energies and surface heterogeneities on the morphology of BCP thin films will be discussed on the basis of the simplest and most studied system, namely thin films of compositionally symmetric, amorphous diblock copolymers. This is followed by a review of BCP thin films for nanopatterning with discussion centering on fabrication of long-range ordered nanostructures of BCP thin films by applying various external fields.

2. Morphologies of BCP Thin Films

2.1. Effect of Confinement

The presence of a surface or interface can strongly influence the phase behavior, morphology and kinetics of a multicomponent system. Understanding of the influence of boundary surfaces, in particular, commensurability and interfacial interactions, on the morphology of BCP thin films has attracted much attention. Phenomena like

symmetric/asymmetric wetting, surface topographies of “islands” or “holes”, surface-induced ordering, and commensurability have been extensively studied.

Symmetric/Asymmetric Wetting. Consider a thin film of a block copolymer below T_{ODT} . The connectivity of the block means that the film thickness is not arbitrary but rather defined in terms of L_0 .¹⁻¹⁹ For an A-b-B BCP, if A or B preferentially locates at both the surface and substrate interface, i.e. symmetric wetting, then the film thickness, h , is defined by nL_0 where n is an integer. If, on the other hand, different blocks segregate to the interfaces, then the film thickness is given by $(n+1/2)L_0$. So, to a first approximation, a thin BCP film is smooth, only if these constraints are satisfied. In all other cases, a surface topography consisting of islands or holes are seen where the step height is L_0 . Examples of these are shown in the scanning force micrographs in Figure 1. Optical microscopy can also be used where discrete interference colors are seen, corresponding to the different thickness or optical path lengths.

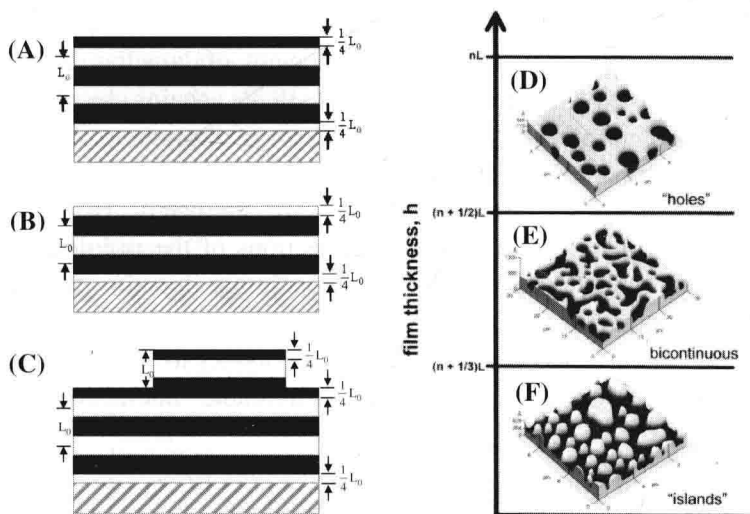


Fig. 1. (A-C) Schematic of three types of film structures. (A) $h = H_n = (n+1/2)L_0$; (B) $h = H_n = nL_0$; (C) $(h = H_n + \Delta h)$. (D-E) AFM images of topographical features of (D) holes; (E) bicontinuous and (F) islands. Reproduced with permission from *Advances in Colloid and Interface Science*.¹⁸

It should be noted that if h is not much different than nL_0 or $(n+1/2)L_0$ for symmetric or asymmetric wetting conditions, respectively, then a surface topography may not be seen and the copolymer chains can stretch or compress to accommodate this incommensurability. This, of course, depends on a balance of the energy associated with stretching or compressing the BCP chains and the additional energy arising from the generation of more surface areas.

Frustration. If the film is confined between two parallel, impenetrable walls, having strong interactions with either A or B block, a surface topography cannot form and the incommensurability between L_0 and h causes a frustration, since the hard boundaries prohibit the formation of surface topography and the characteristic period of BCPs must change to accommodate this frustration. Lambooy et al.^{19, 20} and, subsequently Koneripalli et al.⁶ developed techniques to suppress the formation of surface topography by confining copolymer thin films between two hard walls. Strong interactions of the blocks with the confining walls were sufficient to force the period of BCPs to expand or compress by as much as 50% in some cases. Kickuchi and Binder,^{21, 22} Turner²³ and Walton et al.⁹ theoretically examined the confinement of lamellar BCPs and found that the frustration imposed on BCPs chains by thickness constraints depended strongly on the strength of the interactions of the blocks with the substrate. In the case of strong interactions, stretched or compressed copolymer multilayers were predicted. However, as observed by Lambooy et al.,⁷ as the interactions of the copolymer with the confining walls became weaker, the copolymer domains can change their orientation with respect to the substrate, i.e. orient normal to the wall interface, allowing the period of the copolymer to be L_0 but paying the energetic price associated with unfavorable interaction at the interfaces.

Surface-Induced Instabilities. For $T > T_{ODT}$, if BCPs film is thinner than a characteristic thickness, i.e. $h < h_c$ ($h_c = L_0$ for symmetric wetting and $1/2L_0$ for asymmetric wetting), a "spinodal-like" pattern forms on the surface due to the frustration mentioned above. Prior to the formation of the surface topography, the film is unstable and shows periodic fluctuations.^{18, 24-27} These surface patterns form spontaneously across the

film surface, similar to a film undergoing dewetting. In the BCPs cases, though, the substrate is the initial copolymer layer that is preferentially located at the substrate. When $h = h_t$, the film is stable and the surface remains smooth. For films of $h > h_t$, a layer of thickness $h - h_t$ becomes unstable and dewets an underlying layer of thickness h_t , forming “islands”, “holes” or a “spinodal-like” topography. This type of autophobic dewetting has not been observed in homopolymers.^{18, 28-30}

Surface-Induced Ordering. The presence of a surface can induce ordering of a phase-mixed copolymer, i.e. when $T > T_{ODT}$.^{1, 7, 16, 26, 31-42} This was first predicted by Fredrickson using mean-field theoretical arguments.⁴² Anastasiadis et al. experimentally verified this predication in a neutron reflectivity study on BCPs of polystyrene and poly(methyl methacrylate), denoted PS-*b*-PMMA. By fitting the scattering length density profiles, it was shown that the ordering decays exponentially from the surface with a correlation length very close to the bulk correlation length, in agreement with the arguments of Fredrickson.⁴² Subsequently, Menelle et al.³⁸ studied film thickness dependence of the ordering transition temperature and found that T_{ODT} was significantly elevated by the surface-induced ordering and, in fact, an order-to-disorder transition did not exist in thin films since the order parameter did not decay to zero at any point in the film. However, the films were shown to undergo a transition from a partially to a fully ordered state at a temperature that depended in a power-law manner on the film thickness, as shown in Figure 2.

2.2. Surface Energy

The morphology of BCP thin films is strongly influenced by the strength of interfacial interactions.⁴³⁻⁵⁶ Strong preferential interactions of one block with the substrate or a lower surface energy of one component causes a segregation of that block to either the surface of the film or the substrate interface. As a result, the connectivity of the blocks forces a parallel orientation of the microdomain to the substrate. When the surface is neutral, i.e., the interfacial interactions of both blocks are equally favorable or unfavorable, there is no preferential segregation of

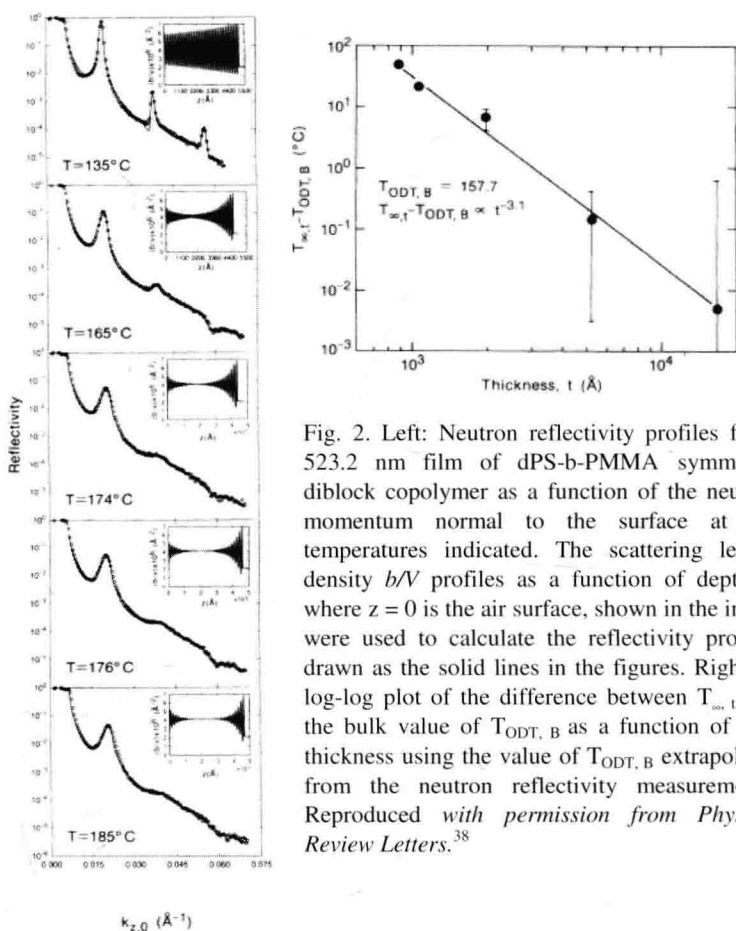


Fig. 2. Left: Neutron reflectivity profiles for a 523.2 nm film of dPS-b-PMMA symmetric diblock copolymer as a function of the neutron momentum normal to the surface at the temperatures indicated. The scattering length density b/V profiles as a function of depth z , where $z = 0$ is the air surface, shown in the insets were used to calculate the reflectivity profiles drawn as the solid lines in the figures. Right: A log-log plot of the difference between $T_{\infty,1}$ and the bulk value of $T_{\text{ODT},B}$ as a function of film thickness using the value of $T_{\text{ODT},B}$ extrapolated from the neutron reflectivity measurements. Reproduced with permission from *Physical Review Letters*.³⁸

the components to the interfaces. Any slight incommensurability will cause the microdomains to orient normal to the surface. The interfacial energies of an A-*b*-B BCP with a solid surface can be precisely controlled by anchoring a random copolymer of A and B, A-*r*-B, to the surface, where the volume fraction, f , of A monomers in the brush can be varied in the synthesis. As f is varied from 0 to 1, the system goes from a condition of preferential wetting of the substrate by A to a preferential wetting by B. However, for one specific value of f the interactions of A and B with the substrate are balanced. This was demonstrated with styrene and methyl methacrylate pairs and it was