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# Ordering in thin films of block copolymers: Fundamentals to potential applications

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ABSTRACT

The ordering of block copolymers in thin films is reviewed, starting from the fundamental principles and extending to recent promising developments as templates for nanolithography which may find important applications in the semiconductor industry. Ordering in supported thin films of symmetric and asymmetric AB diblock and ABA triblock copolymers is discussed, along with that of more complex materials such as ABC triblocks and liquid crystalline block copolymers. Techniques to prepare thin films, and to characterise ordering within them, are summarized. Several methods to align block copolymer nanostructures, important in several applications are outlined. A number of potential applications in nanolithography, production of porous materials, templating, and patterning of organic and inorganic materials are then presented. The influence of crystallization on the morphology of a block copolymer film is briefly discussed, as are structures in grafted block copolymer films.



**Contents**



*Abbreviations:* AFM, atomic force microscopy; GISANS, grazing-incidence small-angle neutron scattering; GISAXS, grazing-incidence small-angle X-ray scattering; HDMS, hexamethyldisilazane; hPB, hydrogenated polybutadiene; HSQ, hydrogen silsesquioxane; $L_0$, (bulk) domain spacing of block copolymer structure; LC, liquid crystal(line); PαMS, poly(α-methyl styrene); PAH, poly(allylamine hydrochloride); PAN, polyacrylonitrile; PaPV, poly(alkoxyphenylenevinylene); P*t*BA, poly(*tert*-butyl acrylate); PBMA, poly(butyl methacrylate); P*n*BMA, poly(*n*-butyl methacrylate); P*t*BMA, poly(*tert*-butyl methacrylate); PBO, (polybutylene oxide)-poly(oxybutylene); PCHE, poly(cyclohexylethylene); PCHEMA, poly(2-(3-cholesteryl-oxycarbonyloxy)ethylmethacrylate); PDXO, poly(1,5-dioxepan-2-one); PE, polyethylene; PEE, poly(ethyl ethylene); PEO, poly(ethylene oxide)=poly(oxyethylene); PEP, poly(ethylene propylene); PFEMS, poly(ferrocenyl ethylmethylsilane); PFS, poly(ferrocenyl dimethylsilane); PGMA, poly(glycidyl methacrylate); PHEMA, poly(hydroxyethyl methacrylate); PI, poly(isoprene); PIOH, hydroxylated poly(isoprene); PIBVE, poly(isobutyl vinyl ether); PLLA, poly(L-lactide); PMAA, poly(methacrylic acid); PMMA, poly(methyl methacrylate); PMB, poly(3-methyl-1-butene); PMS, poly(methylstyrene); P*p*MS, poly(*p*-methylstyrene); PS, polystyrene; PSEB, poly(styrene-*ran*-ethylene-*ran*-butene); P2VP, poly(2-vinylpyridine); RIE, reactive ion etching; SAM, self-assembled monolayer; SAXS, small-angle X-ray scattering; SCF(T), self-consistent field (theory); SEBS, polystyrene-poly(ethylene-co-butylene)-polystyrene; SEM, scanning electron microscopy; SIMS, secondary ion mass spectroscopy; *t*, film thickness; TEM, transmission electron microscopy; TOF-SIMS, time-of-flight secondary ion mass spectroscopy.

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## 1. Introduction

This review is focussed on the ordering of block copolymers in thin films, prepared by spin coating or dip coating methods. In such films, self-assembly of lamellar, cylindrical or spherical domain structures has been extensively investigated for diblock copolymers. These phases also exist in the bulk melt of diblock copolymers [1], although surfaces have a profound effect on ordering, as highlighted herein. The bicontinuous cubic gyroid structure also found in the diblock phase diagram cannot exist in two dimensions. In films of ABC triblocks, other distinct morphologies can exist in two dimensions and what studies there are to date on this are also reviewed.

Potential applications of block copolymer films are now emerging in areas such as high density data storage, nanolithography and others and approaches to achieving technologically useful processing methods with such objectives are discussed in detail.

Ordering in block copolymer thin films has been the subject of a number of previous dedicated reviews [2–6], as well as discussion in a text on block copolymers [1]. Several reviews among these, and others, are focussed on nanopatterning applications [3–5,7–14]. A review on thin films of complexed block copolymers (a topic not considered here) is also available [15]. This is focussed on supramolecular block copolymer (e.g. hydrogen bonded) systems as well as complexes with nanoparticles. A number of reviews have touched on aspects of the theory of ordering in block copolymer films [16,17]. This review covers both experimental and theoretical aspects.