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Optical Metamaterials by Block Copolymer Self-Assembly

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Gyroid Optical Metamaterials James A. Dolan,2018-11-04 This thesis explores the fabrication of gyroid forming block copolymer templates and the optical properties of the resulting gyroid optical metamaterials significantly contributing to our understanding of both It demonstrates solvent vapour annealing to improve the long range order of the templates and investigates the unique crystallisation behaviour of their semicrystalline block Furthermore it shows that gyroid optical metamaterials that exhibit only short range order are optically equivalent to nanoporous gold and that the anomalous linear dichroism of gyroid optical metamaterials with long range order is the result of the surface termination of the bulk gyroid morphology Optical metamaterials are artificially engineered materials that by virtue of their structure rather than their chemistry may exhibit various optical properties not otherwise encountered in nature e g a negative refractive index However these structures must be significantly smaller than the wavelength of visible light and are therefore challenging to fabricate using traditional top down techniques Instead a bottom up approach can be used whereby optical metamaterials are fabricated via templates created by the self assembly of block copolymers One such morphology is the gyroid a chiral continuous and triply periodic cubic network found in a range of natural and synthetic self assembled systems Optical Metamaterials by Block Copolymer Self-Assembly Stefano Salvatore,2014-07-11 Metamaterials are artificially designed materials engineered to acquire their properties by their specific structure rather than their composition They are considered a major scientific breakthrough and have attracted enormous attention over the past decade The major challenge in obtaining an optical metamaterial active at visible frequencies is the fabrication of complex continuous metallic structures with nano metric features This thesis presents the fabrication and characterization of optical metamaterials made by block copolymer self assembly This approach allows fabrication of an intriguing and complex continuous 3D architecture called a gyroid which is replicated into active plasmonic materials such as gold The optical properties endowed by this particular gyroid geometry include reduction of plasma frequency extraordinarily enhanced optical transmission and a predicted negative refractive index To date this is the 3D optical metamaterial with the smallest features ever made **Columnar Structures of Spheres** Jens Winkelmann,Ho-Kei Chan,2023-03-31 Columnar structures many of which are helical refer to dense cylindrical packings of particles They are ubiquitous for example they exist in the contexts of botany foams and nanoscience There have been in depth investigations of columnar structures of both hard spheres e g ball bearings and soft spheres e g wet foams through computer simulations analytic derivations or simple experiments This monograph serves as a comprehensive guide for scientists engineers or artists who would like to have a good grasp of the fundamentals and applications of such aesthetically appealing structures for their own professional interests The book begins with an introduction to the field of packing problems where such problems are closely related not only to the columnar structures presented in the book but also to the structures of condensed matter systems in general It then discusses about columnar

structures of spheres and overviews their classifications and applications It reviews the models and concepts employed in the authors studies on columnar structures of spheres It also details the method of sequential deposition for generating columnar structures of hard spheres computationally or experimentally Lastly it presents some latest findings on the columnar structures of soft spheres and on the structures obtained from the longitudinal compression of a hard sphere chain in a cylindrical harmonic potential *Controlled Self-assembly of Gyroid-forming Block Copolymer Templates for Optical Metamaterials* Karolina Godlewska,2018 **Block Copolymer Photonic Crystals** Jongseung Yoon,2006 Block copolymers have proven to be a unique materials platform for easily fabricated large area photonic crystals While the basic concept of block copolymer based photonic band gap materials has been well demonstrated little work has been achieved yet in terms of realizing optically active devices using these materials n this thesis the utilization of block copolymer photonic crystals for creating self assembled active optical elements has been experimentally explored with a special emphasis on optically driven lasing and stimulus responsive tunable reflectors In pursuing these primary objectives control of thin film microdomain orientation and novel three dimensional 3D optical characterization of block copolymer photonic crystals have been also achieved both of which can greatly help optimize the properties of block copolymer photonic crystals First a laser cavity using block copolymer based one dimensional 1D photonic crystals has been demonstrated Optically pumped surface emitting lasing has been obtained using a dye doped polymers as the organic gain medium and the self assembled block copolymer as the spectral band selective distributed Bragg reflector feedback element **Modeling Self-assembly and Structure-property Relationships in Block Copolymers** Manas Ravindra Shah,2009 Block copolymers have been subject of tremendous research interest owing to their capability of undergoing self assembly which allows them to tailor their electrical optical and mechanical properties Statistical mechanics of flexible block copolymers is well understood However there are many unresolved issues with confinement of block copolymers as well as structure formation in block copolymers having non flexible polymer blocks We develop mean field theory models to address the issues arising in thermodynamics of such complex block copolymers Also we develop theoretical formalisms to understand the link between morphology and macroscopic properties in these block copolymers We study the stability and ordering in thin films of flexible diblock copolymer in the presence of compressible solvent using a combined polymer mean field theory and lattice gas model for binary fluid mixtures We utilize mean field theory model to understand the self assembly behavior in side chain liquid crystalline block copolymers which involve interplay between microphase separation and liquid crystalline ordering of side chain mesogenic units We extend the field theoretic models for block copolymer to account for self assembly in semicrystalline block copolymers The semicrystalline chain is modeled as a semiflexible chain having non bonded attractions between parallel bonds We characterize the structure formation in such block copolymers as a function of the rigidity of the semicrystalline chain Then we extend the formalism to study semicrystalline triblock and pentablock copolymers and

evaluate bridging fractions in different sequences of semicrystalline multiblock copolymers Rod coil block copolymers have a flexible polymer covalently linked to rigid polymer Such polymers have potential applications as organic LEDs and photovoltaic devices We study the self assembly of such block copolymer under confinement To make these block copolymers viable as photovoltaic devices we performed the photovoltaic modeling of devices based on self assembly of block copolymers We characterize the interplay between self assembly and anisotropy of charge transport arising due to rigid polymer chains in determining the eventual photovoltaic properties **Block Copolymers II** Volker Abetz,2005-12-02 A J M ller V Balsamo M L Arnal Nucleation and Crystallization in Diblock and Triblock Copolymers 2 J F Gohy Block Copolymer Micelles 3 M A Hillmyer Nanoporous Materials from Block Copolymer Precursors 4 M Li C Coenjarts C K Ober Patternable Block Copolymers **Block Copolymer Self-assembly and Templating Strategies** Wubin Bai,2016 Block copolymers microphase separate to form periodic patterns with period of a few nm and above without the need for lithographic guidance These self assembled nanostructures have a variety of bulk geometries alternating lamellae gyroids cylinder or sphere arrays tiling patterns core shell structures depending on the molecular architecture of the polymer and the volume fraction of its blocks And in thin films surface interaction and commensurability effect influence the self assembly and result in more diverse morphologies including hexagonal packed perforated lamellae square array of holes The progress of self assembly can be tracked in situ using Grazing Incidence Small Angle X ray Scattering and the annealed morphology can be revealed in 3D using TEM tomography Moreover non bulk morphologies can be produced the ordering of the microdomains can be improved and their locations directed using various templates and processing strategies The blocks can themselves constitute a functional material such as a photonic crystal or they can be used as a mask to pattern other functional materials functionalized directly by various chemical approaches or used as a scaffold to assemble nanoparticles or other nanostructures Block copolymers therefore offer tremendous flexibility in creating nanostructured materials with a range of applications in microelectronics photovoltaics filtration membranes and other devices **Block Copolymer Self-assembly and Co-assembly** Feng Li,2009 **Self-assembly of Block Copolymer Films on Chemically Patterned Surfaces** Richard D. Peters,2001 *Controlling Self-assembly and Anisotropy of Block Copolymer Materials with Nanorods* Castro S. T. Laicer,2007 **Solvent Vapor Assisted Self Assembly of Patternable Block Copolymers** Joan K. Bosworth,2009 Block copolymer self assembly presents a method for patterning and templating applications on the 10 50 nm length scale a smaller scale than can be easily achieved by photolithography Here we investigate the use of functionalized polar nonpolar block copolymers both as photopatternable self assembling materials and for selective infiltration of one block for patterning Block copolymer thin films with defect free self assembled morphology over large domains combined with careful control of the orientation of the morphology are critical for these patterning applications Self assembly of block copolymers is facilitated by polymer chain mobility commonly achieved by heating block copolymer films above the glass transition

temperature of the blocks However many block copolymer systems including those discussed here are thermally incompatible Swelling in a solvent vapor called solvent annealing provides sufficient mobility for self assembly Solvent annealing proved critical to forming ordered structures of functional polar nonpolar block copolymer thin films Thermal instability initially led to limited self assembly of combined topdown bottom up block copolymer systems In this case photolithographic functionality has been designed into block copolymers allowing the majority component of a block copolymer to behave as a negative tone photoresist Solvent vapor annealing has provided a simple and inexpensive method for allowing the bottom up self assembly of these top down photopatternable materials An additional benefit of solvent annealing is the ability to reversibly tune the morphology formed using the selectivity of different swelling solvents to the two blocks that is the choice of solvent for annealing directs the formation of different morphologies in the dried film here spherical and cylindrical This behavior is reversible alternating annealing sessions lead to switching of the morphology in the film Secondary ordering techniques applied in tandem with solvent annealing can be used to further control the self assembly and give highly ordered block copolymer domains Here we demonstrate the use of graphoepitaxy to align block copolymer self assembly to patterns in substrates The combination of block copolymer self assembly with lithographic crosslinking in films was initially pursued to allow precise location of assembled patterns Taking this behavior a step further we combine solvent annealing used to reversibly tune the self assembled morphology and lithographic patterning used to prevent switching in exposed regions This combined process has provided a method for selectively patterning 100 nm wide domains of spherical morphology within regions of parallel oriented cylindrical morphology We also investigate solvent annealing of a block copolymer blended with a hydrogen bonding material that selectively segregates into the polar block Blending provides a method of tuning the periodicity upon solvent annealing for self assembly with morphology control again possible by solvent selectivity Selective extraction of the blended material forms voids displaying the tunable periodicity and the pattern is then transferred by templating to inorganic materials Self-Assembly of Ordered Microporous Materials from Rod-Coil Block Copolymers ,1998 Rod coil diblock copolymers in a selective solvent for the coillike polymer self organize into hollow spherical micelles having diameters of a few micrometers Long range close packed self ordering of the micelles produced highly iridescent periodic microporous materials Solution cast micellar films consisted of multilayers of hexagonally ordered arrays of spherical holes whose diameter periodicity and wall thickness depended on copolymer molecular weight and composition Addition of fullerenes into the copolymer solutions also regulated the microstructure and optical properties of the microporous films These results demonstrate the potential of hierarchical self assembly of macromolecular components for engineering complex two and three dimensional periodic and functional mesostructures *Block Copolymers I* Volker Abetz,2005-11-18 Directed Self-assembly of Block Copolymers and Ternary Block Copolymer/homopolymer Blends on Chemically Patterned Surfaces Into Device-oriented Geometries Mark P. Stoykovich,2007 **Nanostructured Block**

Copolymer Films with Responsive Photonic Band Gap and Nonlinear Optical Properties Yifan Xu,2022 New materials are highly desired for developing next generation photonic devices which can transfer and process information by manipulating light Two properties are usually involved photonic band gap and nonlinear optical response allowing one to guide and modulate light Although many studies have demonstrated these two properties separately it is still relatively unexplored if one can fabricate a single material exhibiting both properties with organic materials Therefore the primary scope of this dissertation work is to study the optical properties of block copolymers that form self assembled morphology and the resulting nanostructure aid in orienting nonlinear optical active crystals with the goal of using this material in future photonic devices This dissertation starts with two independent studies on photonic band gap and nonlinear optical properties in nanostructured polymer materials Firstly a fundamental study on the necessary parameters tuning the resulting photonic band gap properties is designed by using solvent molecules as swelling additives in the self assembled block copolymer nanostructure resulting in a responsive and reversible photonic film Both simulation and experimental results reveal that nanostructure size size distribution effective refractive indices and polymer crystallinity are crucial parameters governing the photonic band gap properties of polymer films Secondly an innovative method is developed to configure dipole moment in the semi crystalline polymer chromophore co crystalline film resulting in significant second order nonlinear optical responses By aligning nonlinear optical active chromophores inside the co crystalline unit cell the dipole moment randomization is avoided leading to a stable material with long term nonlinear optical properties Lastly chromophores are further blended and co crystallized with block copolymers which are expected to form self assembled nanodomains where the optical nonlinearities change alternatingly providing a model material exhibiting photonic band gap and nonlinear optical properties simultaneously Additionally the nanostructure morphology length scale and chemical compositions studied in this dissertation are highly tunable As a result the optical properties of the targeted block copolymer chromophore materials are responsive or even reversible which is yet challenging for inorganic materials Overall introducing polymer materials with both photonic band gap and nonlinear optical properties makes it possible to guide and modulate light simultaneously which would be of interest to apply in future photonic devices and benefit the development of telecommunication networks *Self Assembly of Block Copolymers* Anay Chaube,Massachusetts Institute of Technology. Department of Materials Science and Engineering,2008 cont Block Copolymer self assembly holds great promise in fabrication of such devices requiring periodic high resolution pattern generation If issues such as long range order pattern uniformity and placement accuracy of magnetic dots can be effectively resolved block copolymer self assembly enabled lithography can quickly become the main stay of the multimillion dollar hard disk industry **Self-assembly of Brush Polymers** Benjamin Ragnar Sveinbjörnsson,2014 The unique structure and properties of brush polymers have led to increased interest in them within the scientific community This thesis describes studies on the self assembly of these brush polymers Chapter 2 describes a study on the rapid self

assembly of brush block copolymers into nanostructures with photonic bandgaps spanning the entire visible spectrum from ultraviolet to near infrared Linear relationships are observed between the peak wavelengths of reflection and polymer molecular weights This work enables bottom up fabrication of photonic crystals with application tailored bandgaps through synthetic control of the polymer molecular weight and the method of self assembly Chapter 3 details the analysis of the self assembly of symmetrical brush block copolymers in bulk and thin films Highly ordered lamellae with domain spacing ranging from 20 to 240 nm are obtained by varying molecular weight of the backbone The relationship between degree of polymerization and the domain spacing is reported and evidence is provided for how rapidly the brush block copolymers self assemble and achieve thermodynamic equilibrium Chapter 4 describes investigations into where morphology transitions take place as the volume fraction of each block is varied in asymmetrical brush block copolymers Imaging techniques are used to observe a transition from lamellar to a cylindrical morphology as the volume fraction of one of the blocks exceeds 70% It is also shown that the asymmetric brush block copolymers can be kinetically trapped into undulating lamellar structures by drop casting the samples Chapter 5 explores the capability of macromolecules to interdigitate into densely grafted molecular brush copolymers using stereocomplex formation as a driving force The stereocomplex formation between complementary linear polymers and brush copolymers is demonstrated while the stereocomplex formation between complementary brush copolymers is shown to be restricted Transient Optical Characterisation of Donor-acceptor Block Copolymers for Use in Solar Cells ,2010 Three-dimensional Self-assembly of Brush Block Copolymers to Photonic Crystals Melody Ann Morris,Robert H. Grubbs,Benjamin Sveinbjörnsson,California Institute of Technology. Division of Chemistry and Chemical Engineering,2013 The development of Ring Opening Metathesis Polymerization has allowed the world of block copolymers to expand into brush block copolymers Brush block copolymers consist of a polymer backbone with polymeric side chains forcing the backbone to hold a stretched conformation and giving it a worm like shape These brush block copolymers have a number of advantages over tradition block copolymers including faster self assembly behavior larger domain sizes and much less entanglement This makes them an ideal candidate in the development of a bottom up approach to forming photonic crystals Photonic crystals are periodic nanostructures that transmit and reflect only certain wavelengths of light forming a band gap These are used in a number of coatings and other optical uses One and two dimensional photonic crystals are commercially available though are often expensive and difficult to manufacture Previous work has focused on the creation of one dimensional photonic crystals from brush block copolymers In this thesis I will focus on the synthesis and characterization of asymmetric brush block copolymers for self assembly into two and three dimensional photonic crystals Three series of brush block copolymers were made and characterized by Gel Permeation Chromatography and Nuclear Magnetic Resonance spectroscopy They were then made into films through compressive thermal annealing and characterized by UV Vis Spectroscopy and Scanning Electron Microscopy Evidence of non lamellar structures were seen indicating the first

reported creation of two or three dimensional photonic crystals from brush block copolymers

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    - Chapter 4: Optical Metamaterials By Block Copolymer Self Assembly Springer Theses in Specific Contexts
    - Chapter 5: Conclusion
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