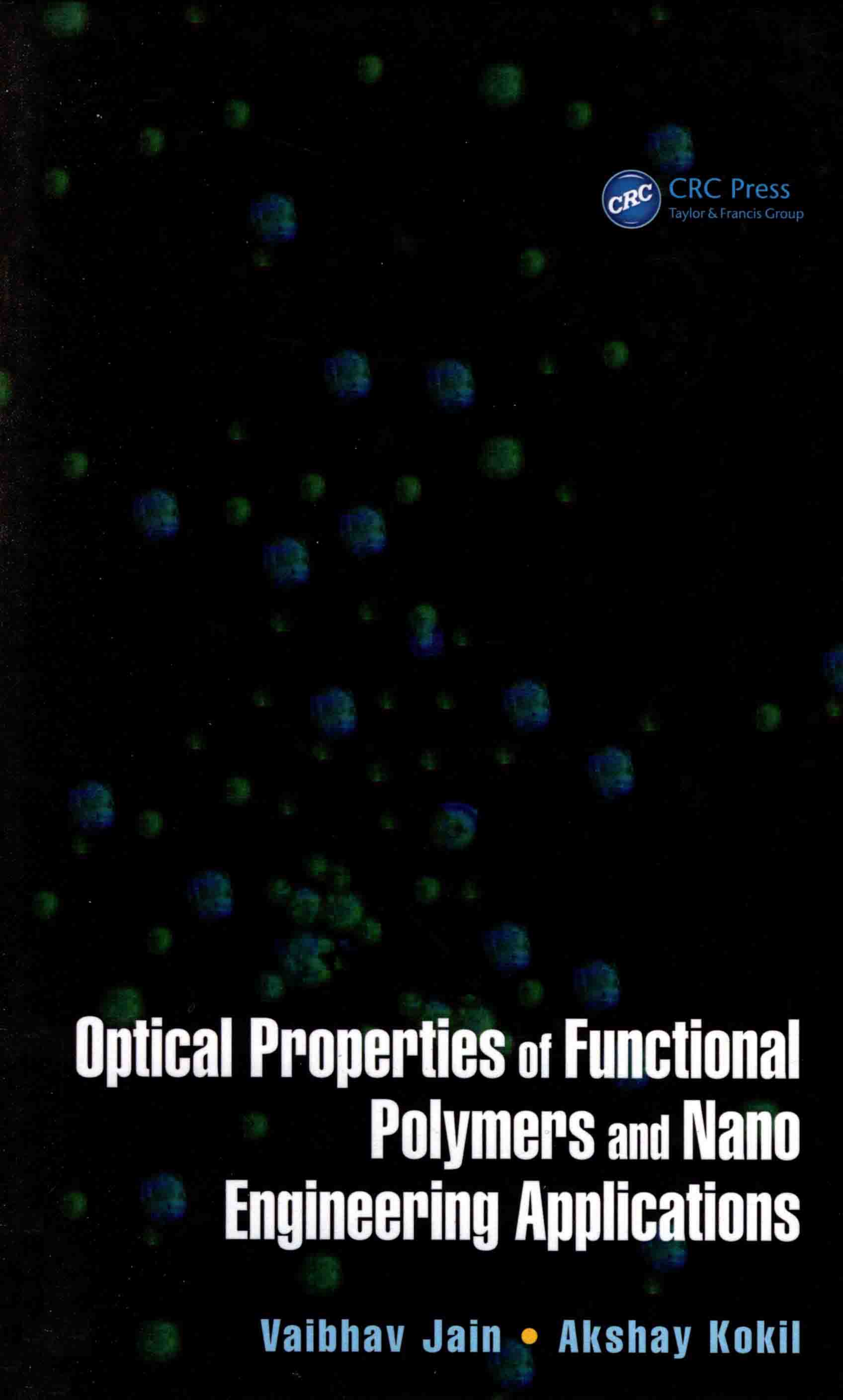

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Optical Properties of Functional Polymers and Nano Engineering Applications

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Optical Properties of Functional Polymers and Nano Engineering Applications

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Optical Properties of Functional Polymers and Nano Engineering Applications

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Optical Properties of Functional Polymers and Nano Engineering Applications, edited by Vaibhav Jain and Akshay Kokil

Preface

Functional polymers offer a unique set of properties according to their chemical structure, even a slight alteration to which brings a significant difference in the material properties of the polymers and hence the applications. The study of their optical properties has emerged as a fast-moving field for nanoengineering applications in scaling up and enhancing various properties of polymers. Although there is literature available to readers that covers the basic optical properties of functional polymers, there has been very little that actually presents a complete and comprehensive overview of the fast-developing field of nanoengineering applications. This book presents a good understanding to readers and gives a basic introduction to the optical properties of polymers, along with providing a systematic overview of the latest developments in their applications in nanoengineering.

The authors have done a tremendous job elaborating on the high-level research along with explaining the basics very well. The introductory chapter (Chapter 1) will broadly discuss the importance of nanoengineering in improving the fundamental optical properties of the functional polymers and will be a preamble for subsequent chapters. Chapter 2 discusses the background and advantages of the liquid gradient refractive index (L-GRIN) lens over the conventional solid lens in various low-cost, reliable medical imaging devices for endoscopy and confocal microscopy. Chapter 3 details photorefractive polymers for 3D display application, providing a good introduction to the electrochemistry of photorefractive polymers, the molecular structure of commonly used polymers, and device manufacturing techniques along with a detailed description of the application of the photorefractive polymers to 3D displays. Chapter 4 focuses on optical gene detection using the optical properties of conjugated polymers. The chapter provides a brief introduction to the physics of fluorescence in photoluminescent polymers, energy and electron transfer mechanisms, along with a detailed explanation of various kinds of DNA sensors.

Chapter 5 contains an introduction to conventional polymer ion sensors based on the optical sensors of conjugated polymers prepared by click chemistry reaction, followed by a detailed explanation of colorimetric visual detection of ion recognition behaviors by using nonplanar donor–acceptor chromophores. Chapter 6 presents details about optical sensors that are based on fluorescent polymers and are used for the detection of explosives and metal ion analytes. Chapter 7 discusses holographic polymer-dispersed liquid crystal technology, its optical setups, and its applications in areas such as organic lasers. Chapter 8 introduces electrochromic phenomena with various organic and organic–inorganic hybrid materials and devices made from them. It presents a detailed background on the research of electrochromic devices, along with new concepts, prototypes, and commercial products available in the market, and future prospects of this technology. Chapter 9, on polymer nanostructures through packing of spheres, demonstrates new techniques for creating nanoscale morphologies through self-assembly, which were not previously possible using known techniques. This approach to assembling polymer nanoparticles into various structures provides distinctive nanoscale morphologies, which in turn affects the optical properties of the functional polymers.

It has been a pleasure working and interacting with the authors and we thank all of them for their efforts. The editors also thank Taylor & Francis for agreeing to publish this book. Special thanks go to Nora Konopka, Joselyn Banks-Kyle, and all of the other supporting staff of Taylor & Francis, Boca Raton, Florida, in producing this book. As editors of this book, we are grateful to the authors, our collaborators, advisers, and colleagues who have provided their valued input and discussions in making this book a success.

Vaibhav Jain
Optical Sciences, Naval Research Lab
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Editors

Dr. Vaibhav Jain currently works in the private industry and is a subject matter expert in materials science and engineering. Before that, he was a materials engineer at the Optical Sciences division at the Naval Research Lab from 2011 to 2013. From 2009 to 2011, he worked in the same division as a National Research Council postdoctoral researcher. Dr. Jain's most recent research focuses on plasmonics, scanning probe microscopy, solar cells, chemical and biological sensors, optical materials, and surface science. He has worked in single-wire spectroscopy to develop electrical contact fabrication on vertically aligned zinc oxide nanowires (NWs) and to investigate them using current-sensing atomic force microscopy (CS-AFM) for photodetectors and solar cell applications. This study also helped in understanding the basic electrical properties of semiconductor NWs with different metals to produce an economical way of developing improved metal–semiconductor contacts (MSCs) for the organic electronics industry.

Dr. Jain received his PhD at Virginia Tech in macromolecular science and engineering in 2009. His graduate research work spans a range of topics in polymer science, applied physics, and optoelectronics, including the fabrication of fast-switching electrochromic devices for flat-panel displays using thin film deposition by layer-by-layer (LbL) and self-assembly techniques, deposition of the nanoparticle stationary phase in microelectromechanical system (MEMS)–based columns for high-speed gas chromatography, and fabricating bending and linear actuators for artificial muscles by LbL assembly. Dr. Jain's expertise also includes synthesizing and characterizing different kinds of nanoparticles (metal nanoparticles, such as Au, Ag, Cu; and inorganics, such as ruthenium purple or Prussian blue), NWs, quantum dots, and depositing thin films from these for a wide variety of applications. He has coauthored 35 publications, one review article, and more than 50 conference presentations. He did his undergraduate education in polymer science and chemical technology at Delhi College of Engineering, New Delhi, India.

Dr. Akshay Kokil is a materials scientist with diverse academic and industrial research experience in design, synthesis, characterization, and processing of novel materials for applications in new technologies. He is actively involved in research on solar cells, organic electronics, sensors, and carbon nanomaterials. He is also experienced in research on environmentally benign synthesis and processing of advanced materials, including electrically conducting, flame-retardant, and self-assembled polymers. He has authored more than 30 publications and 11 conference preprints, and he has presented his research at multiple international research conferences.

Several of his papers have been featured on journal covers and highlighted in research sections of magazines and websites. He is also the author of the book *Conjugated Polymer Networks: Synthesis and Properties* published by VDM Verlag.

Dr. Kokil received a PhD degree in macromolecular science and engineering from Case Western Reserve University, Cleveland, Ohio. He did his undergraduate education in polymer engineering at University of Pune, Pune, India.

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Contents

1

Optical and Optoelectronic Properties of Polymers and Their Nanoengineering Applications

Akshay Kokil and Vaibhav Jain

Polymers consist of multiple small repeating units that are linked together. The small repeating units are called monomers. A number of synthetic strategies have been developed for connecting the monomeric units to obtain the polymers. As expected, the utilized parent monomers govern various properties of the obtained polymers. However, polymers also display a matrix of distinct properties that has resulted in them being widely investigated and utilized in a number of applications. These properties can be tailored by readily altering their chemical structure. The chemical structure of the polymers also has a considerable effect on the organization of the individual polymeric units in bulk, which in turn governs some of the obtained materials' properties.

Along with a number of favorable attributes, the polymers display interesting optical characteristics. Many of the polymers only absorb light in the ultraviolet region, which renders these materials transparent in the remaining visible spectrum. Such transparent polymers have been blended with a number of dyes and pigments to impart distinct photophysical properties to the blend. This has resulted in their utilization in various applications ranging from packaging materials to contact lenses. Alteration of the chemical structure to introduce conjugation in the backbone extends the absorption of light in the visible region and in some cases even the near infrared. On absorption of photons, some of these polymers also emit light as fluorescence or phosphorescence. Owing to their unique chemical structure and photophysical properties, such polymers have been utilized in recent optoelectronic devices and sensors. The underlying principles governing the optical characteristics of polymers are discussed in detail in each chapter of this book.

Confining polymers to nanometer-sized architectures also results in unique properties, which either makes their use in certain applications possible or improves the performance of the applications they are used in. The utilization of architectures on the nanometer scale consisting of polymers with interesting photophysical properties is one of the focuses of this book.

Owing to the difference in their chemical structure, every polymer displays a different refractive index. The organization of the polymer chains in the solid also has a high impact on the refractive index. For example, the refractive index of the crystalline region is different from that of the amorphous region in most of the polymers. If the crystallites are larger than the wavelength of light, the difference in refractive index leads to scattering of light, consequently rendering the polymer either opaque or translucent. The utilization of change of refractive index has been adopted in a variety of applications. Multilayer polymer films, due to the distinct refractive indices of the polymers used in individual layers, display controlled refraction or reflection of the incident light. Chapter 2 discusses in detail the novel application of such gradient refractive index assemblies. The refractive index of the material can also temporarily be altered on application of an external stimulus, such as an intense light beam from a laser source. Such materials have been utilized for applications in holographic displays, which will be discussed in Chapter 3. The use of polymer-dispersed liquid crystals for fabrication of holographic displays is also discussed in Chapter 7.

Polymers that display an alternating sequence of single and multiple bonds in the backbone are called conjugated polymers. Similar to many of the organic dyes, due to the conjugated structure, these polymers display strong absorption of light in the visible region of the electromagnetic spectrum. Many of these polymers are semiconducting and also display emission of light either through fluorescence or phosphorescence. The emission from these polymers can also be altered through various energy/electron transfer processes. The fluorescence in many of the conjugated polymers is dependent on the chemical environment; hence, it has been used as the detectable response in various optical sensors. Multiple analytes such as genes, explosive vapors, metal cations, and corrosive anions have been detected using the change in fluorescence of the conjugated polymers. Such sensors based on conjugated polymers are discussed in Chapters 4, 5, and 6. Because these polymers are semiconducting, application of an external field also causes a change in their photophysical properties such as absorption and fluorescence. Such changes in the optical properties have been utilized in optoelectronic devices, which are also discussed in Chapters 2, 3, 7, and 8.

The fabrication of architectures on the nanometer scale can result in enhancement of performance of many of the applications discussed in this book. Hence, fabrication and assembly of the nanoarchitectures and their utilization in the discussed applications are also presented in Chapter 9.

2

Liquid Gradient Refractive Index Lenses

Yanhui Zhao, Ahmad Ahsan Nawaz, Peng Li, Justin Kiehne, Yuchao Chen, Feng Guo, Xiaole Mao, and Tony Jun Huang

CONTENTS

2.1 Introduction

Optical materials, devices, and systems are vital in many applications in modern technology, from entertainment to consumer electronics to scientific research to medical diagnostics [1,2]. Over the past few decades, much academic and industry attention has been directed at miniaturizing optical systems. Making the optical systems small aims to achieve portability (easily move a device from one location to another), maneuverability (easily change the orientation or configuration of a device), and low cost [3]. Miniaturized optical systems have already found applications in personal electronics (e.g., cameras, cell phones, and tablets), in vivo bioimaging devices such as endoscopes, surveillance/security systems, miniaturized microscopes, and point-of-care diagnostics [4–6].

Most optical systems require precise fabrication, alignment, and actuation of various optical components. This is a challenging enough task at the traditional scale, and has proven to be only more difficult within the constraints enforced by the extremely limited space of miniaturized systems. Thus, in recent years, researchers have been seeking new approaches to the miniaturization of optical systems.

In their efforts to miniaturize optical systems, academics turned to the discipline of microfluidics [7–9]. Years of research effort have yielded a large catalogue of clever microfluidic devices and elements that can manipulate light at the microscale—a discipline now termed optofluidics [10,11]. Some of these elements manipulate light traveling in the device plane [12–14], some manipulate light traveling perpendicular to the device plane [15–17], and others serve to redirect light from a perpendicular path of travel into the device plane [18,19].

This chapter will cover one promising optofluidic component, the polymer (polydimethylsiloxane in specific)-based liquid gradient refractive index (L-GRIN) lens [20,21]. The L-GRIN lens can be readily fabricated via the standard soft-lithography technique and is highly compatible with other microfluidic components. It shows a high tunability and strong focusing performance. The operational flow rate of the L-GRIN lens is on the order of a few microliters per meter, a range two orders of magnitude lower than those in the previously reported microfluidic lenses [22,23]. Such a significant reduction in liquid consumption leads to sustainable operation of the lens and much less stringent requirements in the future on-chip pumping systems for lens control. The L-GRIN lens, which delivers flexibility, performance, and compatibility, will greatly benefit a wide variety of optics-based lab-on-a-chip applications.

2.2 Overview of PDMS-Based Microfluidic Lenses

Generally, microfluidic-based devices are constructed on either silicon or glass substrates, resulting in difficulties in integration of on-chip optical components with the microfluidic systems. Silicon is not a visible-light friendly material, absorbing most light on incidence. Glass, on the other hand, is a transparent material that allows high transmittance for a wide optical frequency range. However, engineering glass microstructures with optical smoothness is extremely challenging. In the past several years, the fabrication or replication of micro- and nanostructures using elastomeric stamps, molds, and conformable photomasks have been enabled with the emergence of soft-lithography techniques [24–28]. Soft lithography has provided a new technical route for the development of polymer-based on-chip optical systems and components. One of the most commonly used polymeric materials for soft lithography is polydimethylsiloxane (PDMS) [29–34]. PDMS has unusual flow properties as a gel material. It can be cured on heating and is optically clear, inert, nontoxic, and nonflammable. With such properties, PDMS is now the most commonly used material for microfluidic channel fabrication. The simple fabrication process and its unique properties provide enormous potential for developing PDMS-based on-chip optical devices,