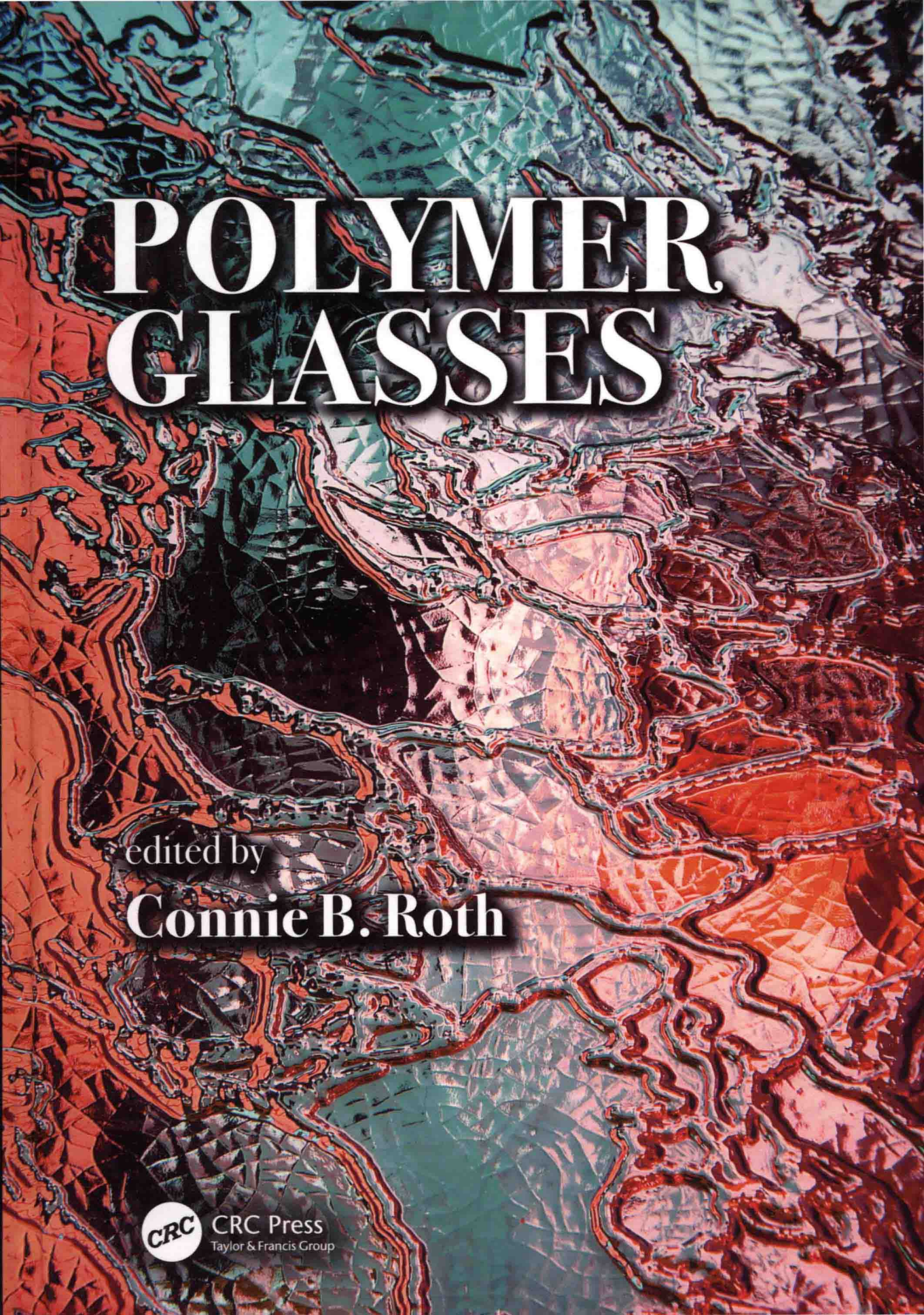
POLYMER GLASSES
edited by
Connie B. Roth
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# POLYMER GLASSES

To all those who simply find joy in learning science.

# Foreword

Understanding the slow dynamics and mechanical response of bulk glass-forming liquids and suspensions (colloids, nanoparticles, molecules, metals, ceramics, polymers, biological matter) remains, as it has been for many decades, a grand scientific challenge of diverse technological relevance. At the heart of the difficulty is understanding strongly activated collective structural rearrangements on the nanometer scale governed by temperature-dependent barriers that are somehow related to Angstrom-scale interactions of the elementary constituents. The most fundamental question is the physical mechanism of vitrification—Is it driven by thermodynamics, structure, and/or purely kinetic considerations? Many diverse, often difficult to reconcile, theoretical proposals coexist in the literature, which range from microscopic to highly phenomenological in character. What is meant by enduring concepts such "cooperative motion" and "dynamic heterogeneity," and whether the latter is of zeroth-order importance for ensemble-averaged structural relaxation, viscosity, and diffusion, remains heavily debated. These issues apply even to the simplified models studied at relatively high temperatures using computer simulation, let alone in the chemically complex venue of deeply supercooled real materials. Conceptual convergence is frustrated by the inability of almost all theories to make quantitative and falsifiable predictions for real systems under the thermodynamic state conditions studied in the laboratory. The possibility remains that the leading order physics depends on material type and/or specific temperature regime probed.

The introduction of interfaces and surfaces modifies glassy dynamics in a spatially inhomogeneous manner with gradients of all dynamical properties induced by nonuniversal interfacial effects and geometric confinement. In engineering applications, glasses are generally used in the nonequilibrium solid state and are often subjected to strong mechanical forces of variable magnitude, symmetry, and temporal history. Additional difficult scientific questions then arise such as the nature of physical aging, deformation-accelerated relaxation and plastic flow, and materials failure. The out-of-equilibrium glass experiences competing driving forces that effectively move it up and down on the potential energy landscape. Boltzmann statistical mechanics no longer apply, presenting a huge challenge for formulating predictive descriptions.

The present book edited by Connie Roth is highly welcome since it provides an excellent snapshot of recent progress on the three broad topics sketched above in the context of arguably the most phenomenologically rich class of glass-forming materials, polymers. Consider first, the structural alpha relaxation in the equilibrated cold liquid. Chemically, one might say that polymers are relatively simple since they are typically constructed from nonpolar monomers. However, they bring much material-specific complexity associated with local conformational flexibility, backbone stiffness, nonspherical monomer shape, tacticity, and chain degree of polymerization. Understanding the most basic question of the mean alpha relaxation time over the typically measured 10–16 decades, and its Arrhenius to supra-Arrhenius evolution with cooling, is an especially large challenge for polymers due to the presence of coupled intra- and interchain degrees of freedom. The richness of polymer chemistry results in remarkably large variations of key dynamical quantities. For example, the glass transition temperature, $T_g$, can be tuned from roughly 150–500 Kelvin for long chains, and the dynamic fragility, which quantifies the rate of increase of the alpha time at kinetic vitrification, varies by nearly an order of magnitude from approximately 25 to over 200. These dynamic properties exhibit chemically specific changes (typically increasing) upon going from oligomers to long chains. This chain length sensitivity can be very large, and potentially provides a unique window on dynamical length-scale effects in the simplifying context of fixed chemistry and intermolecular forces. Although such chemical complexity might be viewed as undesirable from the point of view of comprehending the fundamental physics of glass-forming liquids, it is highly welcome from a materials science perspective, and I believe provides a powerful set of experimental constraints on the development of a predictive and broadly applicable fundamental theory of supercooled liquid dynamics.

A second theme of the book is confinement effects, particularly free-standing (vapor interfaces), supported (one solid, one vapor interface), and capped (two solid surfaces) thin films. The presence of interfaces can speed up or slow down relaxation and transport, and introduces dynamic anisotropy including steep spatial gradients of mobility and mechanical stiffness. The presence of such gradients renders understanding film-averaged properties particularly subtle given the need to average over heterogeneous motion in a manner consistent with the property of interest. Near an interface, polymer chains pack differently, experience a gradient of local density and backbone orientation, and can often strongly physically adsorb via polymer-surface cohesive attractions. These effects locally modify kinetic constraints and hence activation barriers, which are then somehow transmitted into the bulk of the film over surprisingly long distances. Remarkably, the elastic stiffness of the condensed phase boundaries that confine a supercooled liquid also matters, as documented in recent experimental and simulation studies. These fascinating substrate elasticity effects can be surprisingly large. They may be crucial in elucidating whether the alpha relaxation process is associated solely with compact rearranging domains of a few nanometers, or is intimately coupled to the spatially longer-range elasticity that emerges in a cold liquid and the high-frequency mechanical stiffness of confining (solid or liquid) boundaries. All these complexities are, in principle, present for small molecule systems. However, polymers bring qualitatively new scientific aspects, in addition to their practical advantage as excellent thin-film formers. For example, the monomers of a connected polymer chain experience a broad range of friction and local mobility in the spatially heterogeneous film, which modifies its macromolecular diffusivity, length-scale-dependent conformational dynamic modes, and viscoelastic response in a complicated and poorly understood manner.

A third theme of the book, is the below $T_g$ nonequilibrium polymer glass. Even for nondeformed materials, properties are time-dependent due to physical aging, a challenging problem in the bulk and even more so in confined films with mobility gradients. The question of how aging and dynamic heterogeneity are coupled, and how the near-Arrhenius relaxation observed in quenched glasses evolves to supra-Arrhenius behavior at long enough times, is not well understood. Indeed, even the question of whether Arrhenius relaxation can be characteristic of the equilibrated state of some glassy polymers remains debated. When subjected to deformation, the most elementary and foundational question is how the nanometer-scale segmental relaxation process changes. At least four highly nonlinear, coupled processes come into play: external forces can directly reduce effective activation barriers, local structure can become more disordered (sometimes called "mechanical rejuvenation"), the distribution of relaxation times can be strongly distorted, and the physical aging rate becomes stress-dependent. Thus, understanding even the mean segmental relaxation time, its distribution due to dynamic heterogeneity, and the local plastic flow process as a function of stress, strain rate, temperature, aging protocol, and other control variables is a challenging problem in nonequilibrium physics. But again, these issues potentially arise in all glass-forming materials. What is particularly unique about polymer glasses is not only their widespread use as engineering thermoplastics, but the physical consequences of chain connectivity and entanglements on the nonlinear mechanical response. There are many phenomena with an important macromolecular component such as yielding, nonentropic large amplitude strain hardening, fracture, crazing, and the ductile-brittle transition. Addressing them requires confronting the thorny issue of the physical origin of stress, which in polymer glasses subjected to large deformation has both interchain (local forces, nonlocal entanglements) and intrachain origins. Ultimately, a synthesis of ideas from molten polymer rheology with the more solid-state concepts of local activated relaxation and plastic flow in glasses is required to make transformative progress. Addressing these formidable complexities in polymer glasses could be viewed as intractable for fundamental studies, or alternatively as fascinating scientific opportunities with high materials application relevance. Fortunately, polymer scientists adopt the latter perspective, with the present volume providing excellent examples of state-of-the-art efforts in these directions.

In conclusion, the present book will be of great value for both newcomers to the field and mature active researchers by serving as a coherent and timely introduction to some of the modern approaches, ideas, results, emerging understanding, and many open questions in this fascinating field of polymer glasses, supercooled liquids, and thin films.

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# Preface

Polymer glasses have become ubiquitous to our daily life, from the polycarbonate eyeglass lenses on the end of our nose to the large acrylic glass panes holding back the seawater in the Georgia Aquarium tanks. As polymers, they have the advantage of being lighter and easier to manufacture, while possessing the transparency and rigidity associated with glasses. Polymer glasses also have the additional advantage of being ductile, not brittle, after yielding, allowing the material to retain some functionality after failure, instead of disintegrating into a pile of shards. Your plastic water bottle may become dented, but it still holds its water. Given all these important practical uses, polymer glasses have been studied for decades. However, because of the complexities associated with understanding glasses at a fundamental molecular level, modeling properties of polymer glasses have frequently been limited to heuristic approaches.

The challenge with understanding glasses at the molecular level is that they are nonequilibrium materials whose properties depend on many-body interactions. Our traditional statistical mechanics approaches are for equilibrium systems and simple two-body interactions. Investigation of commonalities across different types of glass formers (polymers, small molecules, colloids, and granular materials) has enabled microscopic- and molecular-level frameworks to be developed for these complex systems. Despite their long-chain molecular nature, polymer glasses exhibit many of the same properties as other glass formers because the packing frustration that leads to kinetic arrest and rigidity during glass formation occurs at the segmental level. Thus, theoretical insight from how glass formers are modeled across different systems has led to treatments for polymer glasses with first principle-based approaches and molecular-level detail. These efforts have resulted in improved understanding and agreement between experiment and theoretical modeling that can increasingly be brought to bear on more complicated systems. It is these efforts that the present book aims to summarize and in so doing provide a foundation for research in this field.

The format of the present book has evolved from lively and stimulating sessions that occur yearly at the American Physical Society (APS) March Meeting. In recent years, sessions on polymer glasses have focused on geometrically confined systems such as thin films and on understanding thermo-mechanical deformations and failure mechanisms. Both of these are areas that have many relevant applications driving interest in the field, but are also motivated by fundamental importance. Studies of glass formers in confined geometries strive to access insight on the length scales associated with cooperative motion thought to control the inherent dynamic arrest occurring at the glass transition. The fundamental response of polymer glasses to deformations with different stress and strain stimuli probes the underlying potential energy landscape governing glassy mobility. In the same way that insight from other glass formers has informed our understanding about polymer glasses, studies of polymer glasses represent a rich, well-categorized system for testing theoretical ideas about glass formers in general.

The book is divided into three parts. The first part provides a summary of the fundamental characteristics of polymer glasses, including how they are measured and simulated. The second part covers polymer glasses in confined geometries, while the third part tackles polymer glasses under deformation. The various topics of polymer glasses are covered by experts in these areas: Sindee Simon on the measurement of structural recovery and physical aging (Chapter 2), Jörg Baschnagel on the approaches to computer modeling (Chapter 3), James Caruthers and Grigori Medvedev on the various thermo-mechanical characteristics exhibited by polymer glasses (Chapter 4) and how they are best modeled with various constitutive descriptions (Chapter 14), Connie Roth on the glass transition and physical aging in thin films (Chapter 5), Greg McKenna on the mechanical and viscoelastic properties of thin films (Chapter 6), Koji Fukao on dielectric relaxation spectroscopy studies (Chapter 7), Francis Starr and Jack Douglas on simulating polymers in thin films (Chapter 8), Didier Long on theoretical modeling of glassy thin films and nanocomposites (Chapter 9), Mark Ediger on

measuring enhanced local mobility in deformed glasses (Chapter 10), Jörg Rottler on simulating local relaxations in polymer glasses under stress (Chapter 11), Shi-Qing Wang on the role of chain networks in yielding and failure behavior (Chapter 12), and Rob Hoy on modeling strain hardening (Chapter 13).

I am greatly indebted to all those who have contributed chapters to this book. As the reader will see, the authors went to great lengths to provide extensive summary and perspective of the various topics, explaining both the phenomena as well as providing an outlook for where the outstanding issues still remain. The book is much richer for all their efforts, and it is my hope that this book will provide a starting point for those scientists new to the field of polymer glasses.

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# Editor

**Connie B. Roth** is currently an Associate Professor of Physics at Emory University, as well as the Director of Graduate Studies for the Physics Doctoral Program. She received her Ph.D. and M.Sc. in Physics from the University of Guelph, Canada. Her interest in polymers stems from her time working at Xerox Research Centre of Canada (XRCC) during summers while pursuing her B.Sc. in Physics at McMaster University in Canada. Following postdoctoral positions at Simon Frazier University, Vancouver, and Northwestern University, Chicago, she joined Emory's faculty in 2007. Her research lab studies the physical and mechanical properties of polymer glasses near interfaces, as well as the effects of stress, temperature, and miscibility. She has received a National Science Foundation (NSF) CAREER Award, American Chemical Society PRF Doctoral New Investigator grant, and was the 2009 recipient of the Division of Polymer Physics (DPOLY)/United Kingdom Polymer Physics Group (UKPPG) Polymer Lecture Exchange by the American Physical Society.

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