

1

Introduction

John A. Pojman and Qui Tran-Cong-Miyata

1.1

Overview

We have been friends for almost 20 years, originally drawn together by our seemingly quixotic mission of searching for advantages in studying nonlinear chemical dynamics with polymers. We are excited to have others join us in our quest but it has taken time. A focus issue appeared in *Chaos* in 1999 [1], and then a Conference Proceedings in 2000 [2].

This is the second book we have edited on the topic of nonlinear dynamics and polymers. Our first book appeared in 2003 [3], and it was a collection of symposium papers. Since that time, a great deal of progress has been made, and we chose to make a more focused volume containing invited chapters.

The two audiences for this book are nonlinear dynamicists who are interested in learning about polymers, and polymer researchers who are interested in learning about nonlinear dynamics. The problem of the former is they are unlikely to have a background in polymer chemistry. Polymer researchers are equally unlikely to have knowledge of dynamics.

So how do the ranchers and farmers become friends? We suggest collaboration, and we hope this book can aid such collaborations. A dynamicist can use the examples in the book to identify interesting phenomena and then ask a polymer scientist to help design the systems. Alternatively, a polymer scientist can seek the help of a dynamicist if he or she observes an unusual behavior.

Most of the “usual suspects” of nonlinear dynamics are presented in the following chapters, that is, temporal oscillations, chemical waves, propagating fronts, bifurcation analysis, spatial pattern formation, and the Belousov–Zhabotinsky (BZ) reaction. What distinguishes much of the work in this book from usual nonlinear dynamics is the goal of making some useful materials and devices. However, there is even more that distinguishes the work. New nonlinear phenomena arise in polymers, such as chemomechanical coupling in gel, phase separation induced by periodic forcing, and bistability in permeability.

1.2

What Follows

In Chapter 2, Epstein *et al.* provide an overview of nonlinear chemical dynamics and polymers. They distinguish between “self-assembly,” which is an equilibrium phenomenon, and “self-organization,” which only occurs far from equilibrium and on a much higher length scale. They continue with a discussion of oscillating reactions, chaos, chemical waves, and Turing patterns. They also consider the types of feedback that are known in polymers. Finally, they suggest approaches to creating dynamical systems with polymers.

Most polymeric fluids and solutions are non-Newtonian. Gunes *et al.* discuss the example of one such system in Chapter 3. They focus on the evolution of nonlinear rheological properties during polyurethane network formation in conjunction with the effects of reaction rate, extent of phase separation, diffusion limitations, and mixing protocols, although many of the general features can be readily applied to other polymerizing systems. They selected thermoplastic polyurethanes because of their complicated features; for example, they undergo phase separation and form hydrogen-bonded networks, and their rheological properties evolve during polymerization or even during processing. First, a brief overview of rheological properties of polymerizing systems is presented. This sets the stage for discussion of the rheological changes during polyurethane polymerization and helps in identifying the relationships between morphology and rheology of polyurethanes. Second, they discuss the rheological changes in polyurethanes during polymerization in detail. Third, they present some insight on the mutual relationship between rheology, extent and rate of polymerization, and the nature of the mixing process during polyurethane polymerizations.

This certainly is an important area that nonlinear dynamicists have overlooked, which we hope this contribution will help correct.

Pojman discusses thermal frontal polymerization in Chapter 4. He focuses on thermal frontal polymerization in which a localized reaction zone propagates through the coupling of thermal diffusion and the Arrhenius dependence of the kinetics of an exothermic polymerization. Frontal polymerization is close to commercial application for cure-on-demand applications and is also showing value as a way to make some materials that are superior to those prepared by traditional methods. It also manifests many types of instabilities, including buoyancy-driven convection, surface-tension-driven convection, and spin modes.

These different modes are worth studying because they can significantly interfere with the process. For example, buoyancy-driven convection can destroy a descending front when the polymer is a thermoplastic. Surface-tension-driven convection can quench a front in a thin layer unless the system has a critical viscosity. Nonplanar modes of propagation, called “*spin modes*” because in self-propagating high temperature synthesis (SHS) of inorganic materials, luminescent spots are observed spinning around the front, also appear. Buoyancy-driven convection can affect the appearance of these modes. These spin modes reduce the mechanical strength of the product.

Frontal polymerization can be used to study interesting modes not observable in other systems. For example, spherically propagating fronts can be studied.

Lewis and Volpert continue the discussion of the isothermal form of frontal polymerization in Chapter 5. Isothermal frontal polymerization is also a localized reaction zone that propagates but because of the autoacceleration of the rate of free-radical polymerization with conversion. A “seed” of poly(methyl methacrylate) is placed in contact with a solution of a peroxide or nitrile initiator, and a front propagates from the seed. The monomer diffuses into the seed, creating a viscous zone in which the rate of polymerization is faster than in the bulk solution. The result is a front that propagates but not with a constant velocity because the reaction is proceeding in the bulk solution at a slower rate. This process is used to create gradient refractive index materials by adding the appropriate dopant.

In Chapter 6, Nakanishi *et al.* review phase separation induced by combining photopolymerization with photo-cross-link reactions for a number of photoreactive binary polymer mixtures. The role of reaction inhomogeneity in the mode-selection process in phase separation is demonstrated for a number of binary polymer mixtures using laser-scanning confocal microscopy, light scattering, and Mach–Zehnder interferometry. From these experimental results, the triangular correlations among the reaction kinetics, the resulting transient elastic strain, and the morphological regularity are discussed for mixtures in both liquid and bulk states.

In Chapter 7, Yoshida reviews the work he and his coworkers have carried out to create “intelligent gels” by coupling the catalyst of the BZ reaction to hydrogels. They have created copolymer gels of *N*-isopropyl acrylamide in which ruthenium tris(2,2'-bipyridine) ($\text{Ru}(\text{bpy})_3^{2+}$) is bound to the polymer chain. Gels expand or contract depending on the oxidation state of the ruthenium. They have created self-oscillating gels and self-walking gels. They have also created self-oscillating polymer chains.

Kuksenok *et al.* in Chapter 8 consider self-oscillating gels as biomimetic soft materials. They have modeled systems that exhibit irritability, “the ability to sense and respond to a potentially harmful stimulus.” Specifically, they have modeled materials based on Yoshida’s BZ gel systems that could emit a chemical “alarm signal” and directed motion in response to a mechanical deformation or impact. This could be a significant step to biomimetic materials with important applications.

Boissonade *et al.* consider the chemoelastodynamics of responsive gels in Chapter 9. This chapter is devoted to the spontaneous generation of mechanical oscillations by a responsive gel immersed in a reactive medium away from equilibrium. Two important cases are considered. In the first case, the chemomechanical instability is mainly driven by a kinetic instability leading to an oscillatory reaction. The approach is applied to the BZ reaction. The second case is a mechanical oscillatory instability that emerges from the cross-coupling of a reaction–diffusion process and the volume or size responsiveness of the supporting material. In this case, there is no need for an oscillatory reaction. Bistable reactions, namely, the chlorite-tetrathionate (CT) and the bromate-sulfite (BS) reactions, were chosen

to support this approach. Several theories have been developed to account for gel-swelling mechanisms and their coupling to reactants.

In Chapter 10, Siegel reviews oscillatory systems created with polymer membranes, including membranes that support pressure-, electric-, and chemical-driven oscillations. The interaction of membrane transport with enzyme-catalyzed reactions is also reviewed. Within these systems, feedbacks of various kinds are central to the oscillation mechanisms. In the second part of the chapter, a hydrogel/enzyme system is described that can be used for rhythmic, pulsed delivery of drugs and hormones, driven by a constant external level of glucose, which serves as a free energy source. This system functions by negative, hysteretic feedback between the enzyme reaction and swelling/permeability of the hydrogel.

Steinbock reminds us that polymeric materials need not be organic. In Chapter 11, he examines self-organization in the silica garden system. This fun system is a common demonstration and actually dates back to the seventeenth century. In the conventional “chemical garden” experiment, small salt particles or crystals are seeded into aqueous solutions containing anions such as silicate, carbonate, borate, or phosphate. Such experiments are uncontrolled and cannot be made continuous. Steinbock explains how they replaced the salt crystals by a continuous flow of salt solution. He details the variety of instabilities that can occur and how bubbles can be used as templates for tube growth.

1.3

The Future

We are optimistic about the future of this field, because so much interesting work is present even though only a small fraction of polymer science is represented. We are confident that, as more polymeric systems are explored with the tools of nonlinear dynamics, more exciting and unusual phenomena will be discovered.

We hope this volume will inspire the reader to begin or continue with this new area of research.

References

1. Epstein, I.R. and Pojman, J.A. (1999) Overview: nonlinear dynamics related to polymeric systems. *Chaos*, **9**, 255–259.
2. Khokhlov, A.R., Tran-Cong-Miyata, Q., Davydov, V.A., Kuchanov S.I., and Yamaguchi T. (eds) (2000) *Nonlinear Dynamics in Polymer Science (Polymon '99)*, Wiley-VCH Verlag GmbH, Weinheim.
3. Pojman, J.A. and Tran-Cong-Miyata, Q. (ed.) (2003) *Nonlinear Dynamics in Polymeric Systems*, ACS Symposium Series 869, American Chemical Society, Washington, DC.