FOCUS ISSUE: Nonlinear dynamics related to polymeric systems

Overview: Nonlinear dynamics related to polymeric systems

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I. INTRODUCTION

In the approximately 40 years since the discovery of the Belousov-Zhabotinsky (BZ) reaction, nonlinear chemical dynamics has evolved into a mature area of scientific investigation.[1] Beyond its intrinsic interest, with the amazing array of beautiful phenomena such as oscillations, waves, fronts and spatial patterns, the field has often been heralded for the practical applications it would yield. The relevance to biological and biochemical systems has been a central motivator since the beginning with Belousov's search for a simple analog of the Krebs cycle that led to the discovery of the BZ reaction.[2,3] In at least two areas the payoff appears to be coming. Both control of chaos [Chaos **7**, No. 4 (1997)] and understanding ventricular fibrillation [Chaos **8**, No. 1 (1998)] have been the subject of recent focus issues of this journal.

The preparation of new materials and of current materials in new ways is another promising practical application of nonlinear chemical dynamics. In this issue we focus on nonlinear dynamics related to polymers. Few would contest the importance of polymers in modern life. About half the world's chemists work in polymer-related industries. Surprisingly, relatively little is known about nonlinear phenomena in polymeric systems. One reason for the lack of interest in nonlinear dynamics in polymeric systems may lie in the industrial nature of much of the research. In most industrial processes, nonlinear behavior is seen not as an advantage but as something to be avoided. We hope this Special Issue will change this view.

There are two strategies for exploiting nonlinear dynamics in polymeric systems. The first is to use the intrinsic nonlinearities or feedback in the polymer chemistry. The second is to couple a polymer reaction to another system that exhibits oscillations or pattern formation. As you will see, both strategies have been exploited by the contributors to this issue.

We do not have the space to review polymers but refer the reader to several texts.[4,5] What we seek to provide here is a brief overview of the most important aspects of nonlinearity in polymer systems.

II. EXAMPLES OF FEEDBACK AND NONLINEARITIES IN POLYMERIC SYSTEMS

Direct autocatalysis occurs in biological polymerizations, such as DNA and RNA replication. In normal biological processes, RNA is produced from DNA. The RNA acts as the carrier of genetic information in peptide synthesis. However, RNA has been found to be able to replicate itself, for example, with the assistance of the $Q\beta$ replicase enzyme. Bauer and McCaskill created traveling fronts in populations of short self-replicating RNA variants.[6,7]

Synthetic polymer systems can exhibit feedback through several mechanisms. The simplest is thermal autocatalysis, which occurs in any exothermic reaction. The reaction raises the temperature of the system, which increases the rate of reaction through the Arrhenius dependence of the rate constants. In a spatially distributed system, this mechanism allows propagation of thermal fronts. Free-radical polymerizations are highly exothermic.

Free-radical polymerizations often exhibit autoacceleration at high conversion via an additional mechanism, the isothermal ''gel effect'' or ''Trommsdorff effect.''[8,9] These reactions occur by the creation of a radical that attacks an unsaturated monomer, converting it to a radical, which can add to another monomer, propagating the chain. The chain growth terminates when two radical chain ends encounter each other and terminate. Each chain thus grows only briefly before becoming unreactive. As the degree of polymerization grows, the viscosity increases. The diffusion-limited termination reactions are thereby slowed, increasing the overall rate of reaction. The rate constant of the propagation step is unaffected, because the propagation step involves the addition of a radical to a double bond, a relatively slow process with a rate constant of $\approx 10^4\,(\mathrm{M\,s})^{-1}$. The termination process requires two polymer chains to diffuse together. Once they collide, the radical addition is relatively rapid. As the concentration of polymer molecules increases, the rate of diffusion drops dramatically for both chains. The rate of termination decreases because the polymer chains entangle, but monomers can diffuse through the chains to maintain propagation.

Amine-cured epoxy systems exhibit autocatalysis be-

cause the attack on the epoxy group is catalyzed by OH, and an OH is produced for every epoxy group that reacts.[10,11] The rate of the reaction increases with conversion, but the OH is not liberated, so no propagating fronts can be created.

Some polymer hydrogels exhibit ''phase transitions'' as the pH and/or temperature are varied.[12,13] The gel can swell significantly as the conditions are changed and can also exhibit hysteresis.[14,15]

Almost all polymers are immiscible over some temperature range. Initially miscible solutions of polymers can be made immiscible by a chemical reaction.[16] As the reaction proceeds, the two polymers phase separate, increasing the local concentration of the reacting species.

If two immiscible polymers are dissolved in a common solvent, which is then removed by evaporation, phase separation will occur. If the process is carried out slowly, then an equilibrium structure will result, completely determined by the free energy of mixing. If the solvent is removed rapidly, nonequilibrium patterns may result.[17] Block copolymers consist of distinct sections of immiscible polymers that are linearly connected. Because immiscible components are connected, interesting patterns can form.[18]

Finally, polymer melts and solutions are usually non-Newtonian.[19]

III. NONLINEAR DYNAMICS IN INDUSTRIAL POLYMERIC SYSTEMS

Large industrial reactors are prone to instability because of the slow rate of heat loss that results from the low surface to volume ratio. Because the consequences of an unstable reactor can be disastrous, industrial plants are often operated under far from optimal conditions to minimize the chance of unstable behavior.

Teymour and Ray studied vinyl acetate polymerization in a Continuous-Stirred Flow Tank Reactor (CSTR).[20] The monomer and initiator were flowed into the reactor, which was maintained at a sufficiently elevated temperature for the initiation of polymerization. As the degree of conversion increased, the rate of polymerization increased. The higher rate of reaction meant that the heat produced had less time to dissipate, so the temperature rose. The reaction might have reached a new steady state with higher conversion had the higher temperature not lowered the viscosity. The decrease in viscosity increased the rate of termination. Because these competing processes occurred on different time scales, the system did not reach a steady state, but exhibited temporal oscillations in temperature and conversion. The period of oscillation was long, about 200 minutes, which is typical for polymerization in a CSTR.

The same type of oscillations seen in laboratory-scale reactors has been reported for industrial copolymerization reactors.[21] In a model of vinyl acetate polymerization in an industrial-scale reactor, Teymour and Ray discovered a wide range of dynamical behavior,[22] including a period doubling route to chaotic oscillations. Oscillations in temperature ranged in amplitude from 70 to 140 °C. The extent of conversion oscillated from about 0.5 to almost 1. Obviously,

behavior of this type would be detrimental to the operation of a plant.

Another class of oscillating polymerization reactions in a CSTR was observed in emulsion polymerization.[23,24] In this process, a water-insoluble monomer/polymer is dispersed throughout the aqueous phase with the aid of a surfactant. Potassium persulfate is dissolved in the aqueous phase and thermally dissociates into free radicals that can initiate polymerization when they diffuse into monomer micelles. As the polymer particle grows by incorporating monomer from the micelles, surfactant leaves the aqueous phase to cover the increased surface area of the particle. The surface tension increases with decreasing surfactant concentration. Schork and Ray demonstrated slow oscillatory behavior in the conversion and in the surface tension of the aqueous phase.[23]

Schork and Ray proposed the following explanation. Initially, conversion increases rapidly because new polymer particles are formed and old ones grow. Additional surfactant adsorbs on the increased surface area of the particles. Micelles dissociate as the bulk surfactant concentration falls below the critical level for micelle formation. When all the micelles are gone, no additional polymer particles are formed, so the rate of polymerization slows. The surface tension rises as the aqueous phase is no longer saturated with surfactant. As the particles are washed out of the reactor, the extent of conversion decreases. With the total surface area decreasing and new surfactant flowing in, the surface tension decreases. When the aqueous phase becomes saturated with surfactant, micelles form again, adsorb free radicals and polymerization can commence in them. The process begins anew.

This cycle occurs because there is always enough monomer, but not enough surfactant, to form micelles that can adsorb initiating radicals. The competition between the nonlinear surfactant consumption and the linear rate of surfactant input results in oscillations. Surfactant consumption increases rapidly, as many particles are initiated and grow, but the process overshoots the capacity of the surfactant in the aqueous phase to support polymerization. Once the aqueous phase is no longer saturated, no new particles form, but the old ones continue to grow and consume surfactant. When they are washed out of the reactor and the surfactant saturates the aqueous phase again, new particles can form.

IV. FRONTAL POLYMERIZATION

Thermal autocatalysis can generate propagating fronts, as seen in combustion. The same effect occurs in exothermic polymerization reactions, such as free-radical polymerization and epoxy curing. Frontal polymerization is a mode of converting monomer into polymer via a localized reaction zone that propagates, most often through the coupling of thermal diffusion and Arrhenius reaction kinetics. Frontal polymerization reactions were first discovered in Russia by Chechilo and Enikolopyan in 1972.[25] They studied methyl methacrylate polymerization to determine the effect of initiator type and concentration on front velocity[26] and the effect of pressure.[27] A great deal of work on the theory of frontal polymerization was performed.[28–33] The literature up to 1984

has been reviewed by Davtyan *et al.*[34] The macrokinetics and dynamics of frontal polymerization have been examined in detail[35] and applications for materials synthesis considered.[36]

In stirred reactions, a steady state can lose its stability as a bifurcation parameter is varied, leading to oscillations.[1] Propagating thermal fronts can show analogous behavior. The bifurcation parameter for a thermal front is the Zeldovich number,[37]

$$Z = \frac{T_m - T_0}{T_m} \; \frac{E_{\text{eff}}}{RT_m}.$$

The reaction is assumed to occur in an infinitely narrow region in a single step with activation energy E_{eff}, initial temperature T_0 and maximum temperature T_m.

A great deal of theoretical work has been devoted to determining the modes of propagation that occur.[38–43] In a one-dimensional system, the constant velocity front becomes unstable as Z is increased. A period doubling route to chaos has been shown numerically.[44] A wide array of modes has been observed in self-propagating high temperature synthesis (thermite) reactions.[45]

Begishev *et al.* studied anionic polymerization fronts with ε-caprolactam.[46] A ''hot spot'' moved around the front as it propagated down the tube, leaving a spiral pattern in the product. The entire front propagated with a velocity on the order of 0.5 cm/min, which was a function of the concentrations of activator and catalyst. The hot spot circulated around the outside of the 6 cm [inner diameter (i.d.)] front 16 times as rapidly as the front propagated.

Experimental study of frontal polymerization of methacrylic acid has shown the existence of a rich variety of periodic regimes.[35,47] At ambient initial temperature with heat exchange to room temperature air, only a stable planar front mode exists. Decreasing the initial temperature of the reactants as well as increasing the rate of heat loss leads to the occurrence of periodic modes. The direction of the single-head spinning is arbitrary and can change during front propagation.

Ilyashenko and Pojman studied the single-head spin mode in detail[48] and used previous results of Sivashinsky[42] to build a mode map in the tube diameter-Zeldovich number plane using kinetic data for methacrylic acid fronts. The map shows the expected mode appearance as a function of test tube diameter. They were able to calculate the spiral pitch in good agreement with the experiments.

V. POLYMERIZATION COUPLED TO OSCILLATING REACTIONS

Váradi and Beck[49] observed in 1973 that acrylonitrile, a very reactive water soluble monomer, inhibits oscillations in the ferroin-catalyzed BZ reaction while producing a white precipitate, indicating the formation of free radicals. Pojman *et al.* studied the cerium-catalyzed BZ reaction [ferroin is a poor catalyst because it can complex with poly(acrylonitrile) in a batch reactor].[50] Because poly(acrylonitrile) is insoluble in water, the qualitative progress of the polymerization was monitored by measuring the relative decrease in transmitted light due to scattering of an incandescent light beam passed through the solution. Electron spin resonance (ESR) data show oscillations in the malonyl radical concentration.[51] Oscillations in the bromine dioxide concentration have a greater amplitude ($\approx 10^{-6}$ M) and are out of phase with those of malonyl radical ($\approx 10^{-8}$ M).

Acrylonitrile halts oscillations for a time proportional to the amount added. However, no polymer precipitates until oscillations in both the Pt electrode potential and the bromide concentration return. Then, a white precipitate forms continuously during the oscillations. Even if acrylonitrile in excess of its solubility limit is added, oscillations continue.

Oscillations and polymerization occur in both batch and flow reactors into which acrylonitrile is continuously flowed along with the other BZ reactants. Polymerization occurs periodically, in phase with the oscillations.[50] Washington *et al.* determined that it is not periodic initiation by malonyl acid radicals that causes the periodic polymerization but periodic termination by bromine dioxide.[52]

While these experiments are interesting, it remains to be seen if employing an oscillating reaction to initiate polymerization can be more useful than current approaches.

Yoshida *et al.* created a self-oscillating gel by coupling a pH oscillating reaction with a polymeric gel that expands and contracts with changes in pH.[53]

VI. SPATIAL PATTERN FORMATION

Most polymers are incompatible with one another in the melt and can undergo phase separation, depending on the temperature, mole fractions and molecular weights of each component. As in the case of metallic alloys,[54] there exist two distinct mechanisms for the phase separation of polymer mixtures, the nucleation-and-growth and the spinodal decomposition processes. The former is initiated by large fluctuations in composition (nuclei) whereas the latter proceeds via infinitesimal fluctuations. Though different initially, both processes lead to the same phase equilibrium, resulting in two-phase random morphology.[55] By controlling the kinetics of the spinodal decomposition process, multiphase polymer materials with various co-continuous structures can be designed.

Tran-Cong and co-workers have demonstrated that a wide variety of ordered structures in the micrometer range can be prepared and controlled by photo-crosslinking one polymer component in a binary miscible blend. These materials belong to a class of molecular composites called *semi*-interpenetrating polymer networks (*semi*-IPNs), where the network of one polymer component is formed by appropriate chemical reactions and traps the other polymer component inside. In this work, polystyrene/poly(vinyl methyl ether) (PS/PVME) mixtures were used as polymer blends where the PS chains were labeled with 15 mole percent anthracene. Upon irradiation of the blend in the one-phase region, the anthracenes undergo photodimerization, forming a semi-IPN with PVME trapped inside the PS networks. The morphology resulting from this photo-crosslinking reaction is mainly controlled by the competition between two antagonistic processes, phase separation and photo-crosslinking. By adjust-

ing the strengths of these two interactions via the reaction temperatures and the blend compositions, polymers with co-continuous, labyrinthine, nucleation-assisted spinodal structures and concentric (target) patterns were obtained.[16]

Phase separation of polymer blends under thermally nonuniform conditions is not only an interesting subject related to pattern formation far from equilibrium, but is also crucially important for morphology and/or quality control of many industrial products. Though not popular in polymer materials science, studies of these phenomena have been extensively carried out in the field of metallurgy known as directional solidification.[56,57] Furukawa performed two-dimensional computer simulations for phase separating binary mixtures where the boundary between the stable and the unstable phases was shifted at a constant velocity.[58] Depending upon the magnitude of this velocity, three types of morphology were found. As the shift velocity of the phase boundary decreases, these patterns change from randomly co-continuous structures to undulatory lamella perpendicular to the shifting direction and eventually to columnar morphology parallel to the moving direction of the boundary.

Experimentally, Tran-Cong and co-workers studied the phase separation of a poly (2-chlorostyrene)/poly(vinyl methyl ether) (P2CS/PVME) blend of critical composition in the presence of a temperature gradient.[59] The critical point of the blend was set between the two ends of the temperature gradient. The blend was first allowed to reach phase equilibrium in an initial temperature gradient in order to develop a stationary boundary dividing the stable from the two-phase region. Subsequently, this phase boundary was shifted toward the low temperature side by increasing the temperature gradient. As the front of the boundary propagated, phase separation occurred in the region of the sample with lower temperatures. The phase separation along the temperature gradient was anisotropic. The length scales of the morphology in the direction of the gradient are smaller than those in the perpendicular direction. This structural anisotropy of the blend morphology becomes less pronounced toward the high temperature side. Thus in the presence of a temperature gradient, the length scale and the anisotropy of the phase morphology become functions of the propagation velocity of the phase boundary.

VII. THIS ISSUE

The articles in this issue touch upon many of the phenomena described above. They illustrate a mixture of the most exciting recent advances in theory and experiment.

Yoshida *et al.* study the coupling of chemical and volume oscillations in an oscillatory polymer gel in which the rhuthenium tris (2,2′-bipyperidine) catalyst of the BZ reaction is covalently bonded to the polymer backbone. Leroux and Siegel propose a novel gel oscillator in which hysteresis in the permeability of a copolymer membrane as a function of pH provides the essential feedback for oscillations. Kinoshita *et al.* investigate oscillations in the interfacial pressure in a monolayer of an amphiphilic polypeptide with a β-cyclodextrin end group at n-hexane/water interface.

Hegedus *et al.* studied the behavior of a polymer gel

used to separate alkaline and acidic solutions. The current-voltage characteristics of such a system resemble a semiconductor diode. Tran-Cong *et al.* analyze pattern selection in the phase separation of polymer mixtures driven by two different photochemical reactions, a process that may prove useful for controlling the morphology of multiphase polymeric materials. Karthaus *et al.* investigate the formation of ordered mesoscopic polymer arrays formed by dewetting of a polymer on a substrate.

Ohnishi *et al.* consider analytically the time evolution of phase separation in diblock copolymer melts. Kawaguchi *et al.* carry out experiments on viscous fingering with polymer solutions in linear isotropic and anisotropic Hele-Shaw cells in which air is forced into the solution. Masere *et al.* report new behavior of spin modes in the frontal polymerization of multifunctional acrylates at room temperature. Finally, Barelko and co-workers study frontal polymerization, but with a solid monomer, a cobalt complex of acrylamide. This system supports fronts without any added initiator and allows the preparation of composites by dispersing the monomer on fiberglass cloth.

VIII. QUO VADIS?

The authors in this issue have only touched on the wide array of interesting nonlinear phenomena that can be found in polymeric systems. Diverse as the works are, they all employ one of two basic strategies—utilizing the intrinsic feedback mechanisms and nonlinearities in polymer reactions and systems, or coupling a nonlinear system to a polymeric one. The challenges for the future are to identify additional feedback mechanisms in polymerization reactions and to examine coupling mechanisms between well-studied nonlinear reactions and polymers. This will require that polymer scientists be educated, by themselves or by the nonlinear dynamics community, on the nature of nonlinear dynamics so that they can recognize the potential for their work. Or, perhaps more likely, those who are interested in nonlinear dynamics must learn more about polymers to exploit the enormous potential of these fascinating systems.

ACKNOWLEDGMENTS

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