Macromol. Symp. **160,** *207–214 (2000)*

Nonlinear Chemical Dynamics in Synthetic Polymeric Systems: Motivations and Strategies for Success

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SUMMARY: Two motivations for studying nonlinear chemical dynamics with polymeric systems are considered: observing new nonlinear phenomena and developing new materials because of nonlinearities in polymerization processing. Examples from frontal polymerization are given. Three strategies are considered: coupling polymerizations to nonlinear systems such as oscillating reactions, using inherent nonlinearities in polymerization reactions and investigating the effects of polydispersity on known instabilities.

Introduction

The field of nonlinear chemical dynamics is now a mature area of scientific investigation after approximately forty years 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 justified on the basis of practical applications it would yield. The preparation of new materials and current materials in new ways is a promising application of nonlinear chemical dynamics (NLCD). Most of the work done in studying nonlinear phenomena in polymeric systems has been related to identifying instabilities in industrial processes with the goal of avoiding them. Epstein and Pojman reviewed some of this work 1). However, there are many investigators now looking at nonlinearities with polymers, not as phenomena to be shunned but rather sought out and embraced. A recent issue of the journal *Chaos* was dedicated to nonlinear dynamics and polymeric systems 2), and Pojman recently considered self organization in synthetic polymeric systems 3).

Strategies

There are at least three strategies for exploiting nonlinear dynamics in polymeric systems. The first is to couple a polymer reaction to another system that exhibits oscillations or pattern

CCC 1022-1360/00/$ 17.50+.50/0

formation. Excellent examples are the works of Yoshida and his co-workers in coupling pH oscillators and the Belousov-Zhabotinsky reaction (BZR) with gels. If a pH sensitive gel is present in a pH oscillator, the gel periodically expands and contracts in phase with the pH oscillations 4). By incorporating the ruthenium catalyst into a gel that is sensitive to its oxidation state, periodic expansions and contracts can be observed in the BZR 5).

Another example is the periodic polymerization of acrylonitrile when added to the (BZR). Váradi and Beck 6) 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) 7). 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. Polymerization occurs periodically, in phase with the oscillations 7). 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 8). 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.

We attempted to produce propagating polymerization fronts by adding acrylonitrile to chemical waves in the BZR. Unfortunately, the system is immediately transformed from the reduced to the oxidized state without wave propagation. We also considered using a pH front to create a redox initiation front but adding acrylonitrile to the chlorate-sulfite front system 9) suppressed front propagation. Most likely essential free-radical intermediates were scavenged by the acrylonitrile. A strategy to avoid this problem is to develop a pH front based on enzyme chemistry. Zoltan Noszticzius suggested using urease, which converts urea to ammonia. Ureases have low activity at low pH and so a system initially at low pH might support a front if initiated with a drop of ammonia solution. If a redox initiating system that is inactive at low pH but active at high pH is coupled to such an enzyme-catalyzed front, an isothermal polymerization front could be developed.

The second strategy is to use intrinsic nonlinearities or feedback in polymer chemistry. Synthetic polymer systems exhibit feedback through several ways. The simplest is thermal autocatalysis. In a spatially distributed system, this mechanism allows propagation of thermal fronts. Free-radical, amine- or cationically-cured epoxies, ring-opening metathesis and ionic polymerizations are very exothermic. Condensation polymerizations are not.

Isothermal autocatalysis, which is so prevalent in inorganic systems, is rare in polymerization chemistry, except for the "gel effect" 10, 11). There are two schemes we can imagine for achieving it. The first is that a small molecule, X, is liberated when the monomer adds to the growing chain, and this species catalyzes the chain growth.

$$P_n * + M \rightarrow P_{n+1} * + X ; \qquad \frac{d[M]}{dt} = -k[P *][M][X]^m$$

The second possible way would be for chain branching in which an additional propagating center is created.

$$P_n * + M \rightarrow P_{n+1} * + P_1 * ; \qquad \frac{d[M]}{dt} = -k[P \bullet][M][X]^m$$

The closest that has been observed is the copolymerization with oxygen and an inhibitor in which hydroperoxy radicals are formed that can cleave and initiate new chains. When styrene has been polymerized with oxygen and phenols, oscillations have been observed 12, 13).

Amine-cured epoxy systems exhibit autocatalysis because the attack on the epoxy group is catalyzed by OH, and an OH is produced for every epoxy group that reacts 14, 15). The rate of the reaction increases with conversion, but the OH is not liberated so no propagating fronts can be created.

Some polymer hydrogels can swell significantly as the conditions are changed 16) and exhibit hysteresis in permeability 17). Siegel presented preliminary evidence that coupling a gel, poly(*N*-isopropylacrylamide-*co*-methacrylic acid), having hysteresis in the permeability as a function of pH with the glucose oxidation reaction can produce an oscillating reaction if glucose is in the surrounding medium 18). Such a system could be used for periodic drug delivery.

The last feedback mechanism that has been used is based on the fact that almost all polymers are immiscible over some temperature range. Initially miscible solutions of polymers can be made immiscible by a chemical reaction 19). As the reaction proceeds, the two polymers phase separate, increasing the local concentration of the reacting species.

The third strategy, suggested to the author by A. Khokhlov, is to investigate the effects of polydispersity on known instabilities. Pojman et al. analyzed the problem of ester interchange reactions in an unstirred system 20). An initially equilibrium distribution of polymer lengths immediately becomes nonequilibrium because the diffusion coefficients are length dependent. If interchange reactions are occurring, they can bring the system back to a local equilibrium,. Pojman et al. considered a one-dimensional system in which the average length and the concentrations at the boundaries were fixed. The resulting steady states revealed a nonlinear distribution of molecular concentration and mass. The entropy of the polymer distributions was calculated as function of position and shown to be less than the entropy for the distributions without interchange reactions. Thus the polydispersity coupled with reaction and diffusion created a spatial structure, although a rather trivial one.

Motivation 1: Making New Materials

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 21). The literature up to 1984 was reviewed by Davtyan et al. 22) The macrokinetics and dynamics of frontal polymerization have been examined in detail 23) and applications for materials synthesis considered 24).

Because of the rapid conversion in the reaction zone, novel thermochromic composites have been prepared 25) as well as unique polymer blend morphologies 26) and uniform copolymers 27). Chekanov and Pojman developed a frontal polymerization method to produced Functionally Gradient Materials (FGM) in which the composition can be externally programmed 28). The frontal curing of epoxy resins can produce some superior materials without curing ovens 29, 30).

Isothermal frontal polymerization (IFP) occurs when a polymer seed, i.e., a piece of polymer, is placed in contact with a solution of its monomer (usually methyl methacrylate, MMA) and a

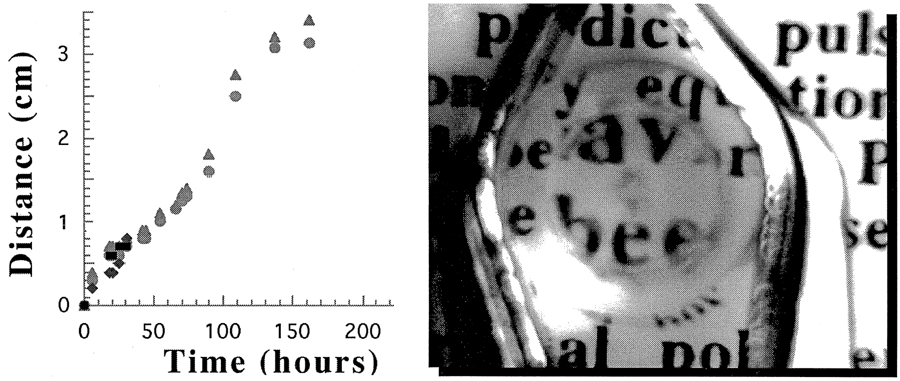

Fig. 1. Left: Propagation of MMA polymerization front with lauroyl peroxide at 70 °C without an inhibitor. Two experiments are plotted together. Data courtesy of Lydia Lewis. Right: A GRIN lens (1.5 cm diameter) of poly(methyl methacrylate) with naphthalene as the dopant. Notice how the text is magnified. Image courtesy of Victor Ilyashenko.

thermal initiator. The monomer swells the seed, and polymerization occurs faster in the swelled gel than in the bulk medium because of the gel effect. (The high viscosity slows termination reactions in free-radical polymerization without significantly affecting the rate of chain growth.) The interface propagates about 1 cm/day 31, 32). This technique is also called Interfacial Gel Polymerization by Koike 33). Fig. 1 shows the position versus time for a front in MMA and that the front does not have a constant velocity. The velocity increases because the viscosity in the bulk monomer increases slowly until the entire medium rapidly polymerizes. Volpert and Spade have modeled this process 34). If a dopant is present in the seed, or in the monomer/initiator solution, Gradient Refractive Index (GRIN) materials can be produced 35). Fig. 1 also shows a flat disk composed of poly(methyl methacrylate) in which naphthalene was dissolved in the methyl methacrylate/lauroyl peroxide solution. An annulus of polymer was filled with that solution, and the sample cured at 40 °C. The dopant accumulates in the solution as the front propagates, increasing the refractive index toward the center. Such a sample can be pulled into GRIN fiber for use in high-bandwidth communication networks 36).

Motivation 2: Observing New Nonlinear Phenomena and Instabilities

No doubt many new phenomena can be found in polymer systems but we consider a few examples with frontal polymerization. Splendid periodic modes of frontal propagation have been studied in Self-Propagating High Temperature Synthesis (SHS) [37, 38]. These systems can be rather difficult to study because of the high temperature (1000 °C), high front velocities (m/s) and expensive materials. Frontal polymerization experiments are much easier to study with temperatures on the order of 200 °C, velocities on the order of 1 cm/min and inexpensive reagents [23]. Also, because liquid monomers can be used, convective phenomena in thermal fronts can be investigated [39]. Free-radical polymerization is non-stoichiometric and so the velocity of the front can be varied without significantly altering the front temperature.

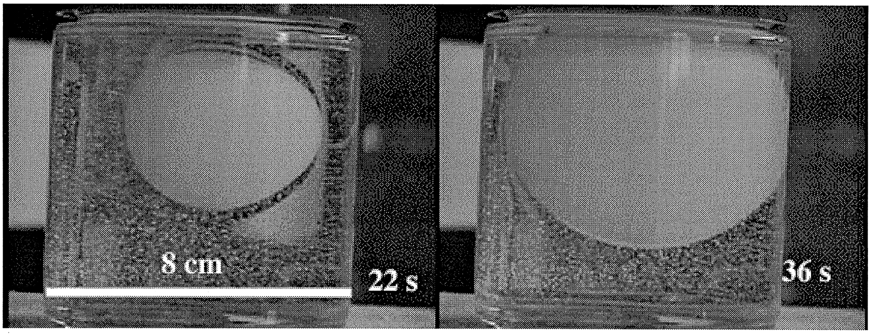

Fig. 2. A front propagating in a solution of 1,6 hexanediol diacrylate (40%) and DMSO (60%) with CAB-O-SIL (ultrafine silica gel, 6.7% w/v). Ammonium persulfate was the thermal initiator and Irgacure 184 the photoinitiator. Courtesy of Marcus Molden.

Thermal fronts have been studied in cylindrical geometries but because the materials used in SHS are opaque, spherically-propagating fronts can not be studied. Using a diacrylate/silica gel mixture (to prevent convection), we produced such fronts by igniting the front by illuminating with UV light. A small amount of photoinitiator had been injected in the center (Fig. 2). Notice the opaque front propagating outward. Such a system has only been seen using polymers and provides the opportunity to observe new phenomena in thermally-propagating fronts. Observing how spin modes manifest themselves in such systems will be most interesting.

Conclusions

Nonlinear phenomena can be found with synthetic polymeric systems by coupling them to nonlinear systems such as oscillating reactions, by using inherent feedback mechanisms, such as thermal autocatalysis and the gel effect, or because of the dispersity of molecular weights.

Two motivations are the development of new materials and the opportunity to observe new nonlinear phenomena.

Acknowledgements

This work was supported by NASA's Microgravity Materials Science Program (NAG8-1466) and by the US Office of Naval Research.

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