NONLINEAR CHEMICAL DYNAMICS IN SYNTHETIC POLYMER SYSTEMS

John A. Pojman[*]
*Department of Chemistry, Louisiana State University,
Baton Rouge, LA 70803*

Abstract. The application of the methods of nonlinear chemical dynamics to synthetic polymer systems is considered. We review the differences between polymers and inorganic systems that have been the subject of nonlinear dynamics. We consider two methods for approaching the problem – coupling polymers to other nonlinear systems and using inherent nonlinear behavior of polymers. We specifically focus on frontal polymerization.

Keywords: autocatalysis, feedback, frontal polymerization

1. Introduction

What is to be gained from applying the methods and concepts of nonlinear dynamics to polymer systems? Are there things that nonlinear dynamicists can learn, or that polymer scientists can make, that would not be possible without bringing these two apparently disparate fields into contact? First we briefly review some distinguishing characteristics of polymers. Next, we suggest three challenges that present themselves. We then examine sources of feedback in polymeric systems. Next, we propose several approaches to develop nonlinear dynamics with polymers. Finally, we give some examples of results that suggest that these approaches are likely to bear fruit.

We do not have the space to review polymers but refer the reader to several texts [1–3]. What we seek to provide here is a brief overview of the most important differences between polymeric systems and small molecule ones, review sources of feedback, approaches to nonlinear dynamics with polymers, including some specific examples.

We will not deal with biological systems, which certainly are polymeric systems. Biological systems are nonlinear dynamical systems but they are complex enough and so important that they warrant separate treatment. We refer the reader to Goldbeter's book [4] for an introduction to the topic.

---

[*] To whom correspondence should be addressed. e-mail: john@pojman.com

1.1. WHAT IS SPECIAL ABOUT POLYMERS?

The distinguishing feature of polymers is their high molecular weight. The simplest synthetic polymer consists from hundreds to even millions of a single unit, the monomer, that is connected end to end in a linear chain. However, a distribution of chain lengths always exists in a synthetic system. The molecular weight distribution can be quite broad, often spanning several orders of magnitude of molecular weight.

Linear polymers, are often *thermoplastic*, meaning they can flow at some temperature, which depends on the molecular weight, e.g., polystyrene. Polymers need not be simple chains but can be branched or networked. Crosslinked polymers can be gels that swell in a solvent or *thermosets*, which form rigid 3-dimensional networks when the monomers react, e.g., epoxy resins. This interconnectedness allows long-range coupling in the medium.

The physical properties of the reaction medium change dramatically during reaction. For example, the viscosity almost always increases orders of magnitude. These changes often will affect the kinetic parameters of the reaction and the transport coefficients of the medium.

Phase separation is ubiquitous with polymers. Miscibility between polymers is the exception.

1.2. CHALLENGES

In contemplating the possible payoffs from applying nonlinear dynamics to polymeric systems, one might ask

1. Are there new materials that can be made by deliberately exploiting the far-from-equilibrium behavior of processes in which polymers are generated?
2. Are there existing materials and/or processes that can be improved by applying the principles and methods of nonlinear dynamics?
3. Are there new nonlinear dynamical phenomena that arise because of the special properties of polymer systems?

2. Sources of feedback

In order to observe the types of nonequilibrium self-organization seen with inorganic systems such as the Belousov-Zhabotinsky reaction (see Epstein and Pojman for a discussion [5]), the polymer systems must exhibit feedback. 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 of certain monomers exhibit autoacceleration at high conversion via an additional mechanism, the isothermal "gel effect" or "Norrish-Trommsdorff effect" [6–9]. 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 chains ends encounter each other, forming a stable chemical bond. As the polymerization proceeds, the viscosity increases. The diffusion-limited termination reactions are thereby slowed down, leading to an increase in the overall polymerization rate. The increase in the polymerization rate induced by the increase in viscosity builds a positive feedback loop into the polymerizing system.

The reaction of dianhydrides with diamines can follow autocatalytic kinetics if performed in the proper solvent [10]. The reaction of the amine with the anhydride creates a carboxylic acid that catalyzes reaction of the amine with an anhydride. 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 [11–13]. The synthesis of polyaniline by oxidation of aniline has been shown to be autocatalytic, if performed electrochemically [14] or by the direct chemical oxidation [15,16]. Because polymerization reaction are organic reactions, more study should be made of autocatalysis in organic synthesis.

Some polymer hydrogels exhibit "phase transitions" as the pH and/or temperature are varied [17,18]. The gel can swell significantly as the conditions are changed and can also exhibit hysteresis [18,19].

Most polymers are not miscible. Introducing chemical reactions to an initially miscible polymer mixture often leads to phase separation [20]. Autocatalytic behavior driven by chemical reactions and concentration fluctuations in miscible polymer mixtures was recently found in photo-cross-linked polymer mixtures [21]. Concentration fluctuations increase as the reaction proceeds, leading to the condensation of photoreactive groups labeled on one of the polymer components. This condensation leads to an increase in the reaction yield that, in turn, accelerates the concentration fluctuations. A positive feedback can thus be built in the reacting mixture under appropriate conditions.

If two immiscible polymers are dissolved in a common solvent, which is then removed by evaporation, phase separation will occur. If the solvent is removed rapidly, non-equilibrium patterns may result [22].

The necking phenomenon observed upon stretching a polymer film at a constant temperature is a well-known consequence of a negative feedback loop driven by the interplay between the increase in temperature

associated with the sample deformation and its glassification caused by the heat exchange with the environment [23]. Oscillatory behavior and period-doubling in the stress resulting from a constant strain rate have been experimentally observed.

Diffusion of small molecules, usually solvents, into glassy polymers exhibits "anomalous" or "non-Fickian" behavior [24]. As the solvent penetrates, the diffusion coefficient increases because the glass transition temperature is lowered. The solvent acts as a plasticizer, increasing the free volume and the mobility of the solvent. Thus we have an autocatalytic diffusion process. This can be relevant in Isothermal Frontal Polymerization, which we discuss below.

Dissolving of some polymers in aqueous media can proceed by a front [25]. Water dissolvable polymers are formed from esters, which create an acid upon hydrolysis that can catalyze further hydrolysis.

Finally, polymer melts and solutions are usually non-Newtonian fluids [26–28]. They often exhibit shear thinning, which means the viscosity decreases as the shear is increased. This can lead to unusual phenomena. For example, when a polymer melt is extruded through a die, transient oscillations can occur [29,30]. (Polymers can also exhibit shear thickening.)

An unusual phenomenon is the Weissenberg effect, or the climbing of polymeric liquids up rotating shafts [28]. A Newtonian fluid, on the other hand, is depressed by rotation because of centrifugal forces.

3.   Approaches to nonlinear dynamics in polymeric systems

We propose three approaches to creating nonlinear dynamical systems with polymers:

- Couple polymers and polymer-forming reactions to other nonlinear systems (Type I)
- Create a dynamical system using the inherent nonlinearities in polymeric systems (Type II)
- Polymer systems are invariably characterized by polydispersity of the molecular weight distribution. One should be able to exploit the distribution of polymer lengths to amplify nonlinear effects in polymer systems, perhaps because of the molecular weight dependence of the diffusion coefficient. We know of no experimental work but there has been a theoretical work considering such an effect on ester interchange reactions [31].
- Investigate the effects of reaction-dependent diffusion coefficients on known instabilities.

3.1. TYPE I: COUPLING TO ANOTHER NONLINEAR SYSTEM

3.1.1. *Nonlinear chemical system*

Given the importance of the BZ reaction in nonlinear chemical dynamics, it is not surprising that polymers and polymerizations would be coupled to it. Váradi and Beck had shown that adding acrylonitrile to the BZ reaction could inhibition oscillations and a precipitate was produced that they assumed was polyacrylonitrile [32]. Pojman et al. studied the BZ reaction to which acrylonitrile was added and showed that, after an inhibition period, the polyacrylonitrile was produced periodically in phase with the oscillations (Figure 1) [33]. Given that radicals are produced periodically from the oxidation of malonic acid by ceric ion, it seemed reasonable to assume the periodic appearance of polymer was caused by periodic initiation. However, Washington et al. showed that periodic termination by bromine dioxide caused the periodic polymerization [34].

An exciting application of coupling to another nonlinear system was demonstrated by Yoshida et al. who created a self-oscillating gel by coupling a pH oscillating reaction with a polymeric gel that expands and contracts with changes in pH [35]. They have also used a gel in which the ruthenium catalyst of the BZ reaction is chemically incorporated into polymer [36,37]. Yashin and Balazs have also considered the coupling of the BZ system to gels [38,39].
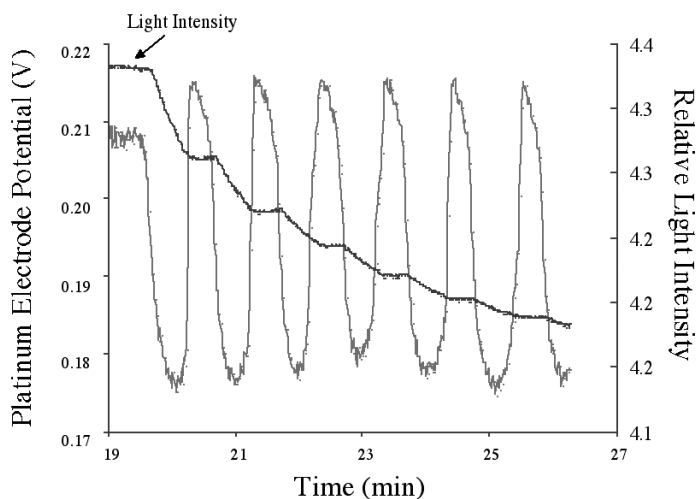

Figure 1. The evolution of a BZ reaction in which 1.0 mL acrylonitrile was present before the Ce(IV)/H_2SO_4 solution was added. [NaBrO$_3$]$_0$ = 0.077 M; [Malonic Acid]$_0$ = 0.10 M; [Ce(IV)]$_0$ = 0.0063 M; [H_2SO_4]$_0$ = 0.90 M. No oscillations occurred the first 15 min. (Adapted from [33].)

3.1.2. *Convective systems*

The nonlinear system need not be a chemical reaction. Kumacheva has used buoyancy-driven convection to generate patterns and then fixes them with polymerization [40,41]. Karthaus has used solvent dewetting to create micrometer sized domes of polymer on a solid substrate [42].

There is not always a clear distinction between Type I and Type II systems. In some cases the nonlinearities of the gel also play a role. Gauffre et al. and Labrot et al. have found that "if spatially bistable reaction systems are operated in size responsive chemosensitive gels, the size changes can provide a feedback which beyond plain reaction diffusion instabilities can be the source of new self-organizing phenomena, referred to as chemo-mechanical structures." [43–46]. Siegel and his colleagues utilized the hysteresis in a hydrogel's permeability to create autonomous chemomechanical oscillations in a hydrogel/enzyme system driven by glucose [47,48].

3.2. TYPE II: USING THE INHERENT NONLINEARITIES IN A POLYMER SYSTEM

3.2.1. *Oscillations in a CSTR*

With their combination of complex kinetics and thermal, convective and viscosity effects, polymerizing systems would seem to be fertile ground for generating oscillatory behavior. Despite the desire of most operators of industrial plants to avoid nonstationary behavior, this is indeed the case. Oscillations in temperature and extent of conversion have been reported in industrial-scale copolymerization [49].

Teymour and Ray reported both laboratory-scale CSTR experiments [50] and modeling studies [51] on vinyl acetate polymerization. The period of oscillation was long, about 200 min, which is typical for polymerization in a CSTR. Papavasiliou and Teymour reviewed nonlinear dynamics in CSTR polymerizations [52].

Emulsion polymerization as well has been found to produce oscillations in both the extent of conversion and the surface tension of the aqueous phase [53].

3.2.2. *Spatial pattern formation*

Typical phase separation leads to a two-phase disordered morphology. Multiphase polymeric materials with a variety of co-continuous structures can be prepared by controlling the kinetics of phase separation via spinodal decomposition using appropriate chemical reactions. By taking advantages

of photo-crosslinking and photoisomerization of one polymer component in a binary miscible blend, Tran-Cong-Miyata and coworkers [54,55] have been able to prepare materials, known as semi-interpenetrating polymer networks, and polymers with co-continuous structures in the micrometer range.

4. Frontal polymerization

Frontal polymerization (FP) is a process of converting monomer into polymer via a localized reaction zone that propagates through the monomer. There are three modes of FP.

4.1. ISOTHERMAL FRONTAL POLYMERIZATION

Isothermal Frontal Polymerization (IFP), also called Interfacial Gel Polymerization, is a slow process in which polymerization occurs at a constant temperature and a localized reaction zone propagates because of the gel effect [56,57]. Figure 2 shows an image of a Gradient Refractive Index lens prepared by IFP.

Lewis et al. studied the mechanism of IFP with methyl methacrylate using Laser Line Deflection to determine front position and the front profile [58] and determined the factors that affect front propagation [59] Evstratova et al. confirmed that the process is indeed isothermal [60].

Figure 2. An image of a GRIN lens created by a radially-propagating front of methyl methacrylate polymerization from an annulus (1.5 cm) of poly(methyl methacrylate). Naphthalene was initially present in the monomer and accumulated as the front propagated inward.

Figure 3 presents a schematic of the mechanism. IFP proceeds as follows: Monomer and initiator dissolves into a polymer "seed", i.e., a high molecular weight piece of poly(methyl methacrylate). Because of the gel effect, the rate of polymerization is much faster in this viscous region than in the bulk solution. However, we must remember that the initiator is decomposing throughout the solution and so polymerization is occurring everywhere. It is also possible to add a polymeric inhibitor to extend the time of propagation [57]. Figure 4 shows a typical front's position as a function of time, for three different temperatures.

There are three distinct features of IFP. First, the total propagation distance is small. Secondly, the velocity is also very small and not constant. The propagation stops when the entire solution has polymerized. The front accelerates because polymerization is still occurring in the monomer-initiator solution away from the seed. The viscosity in the bulk solution is thus increasing slowly.
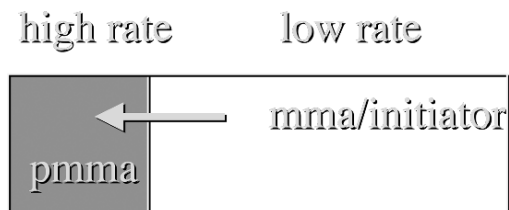

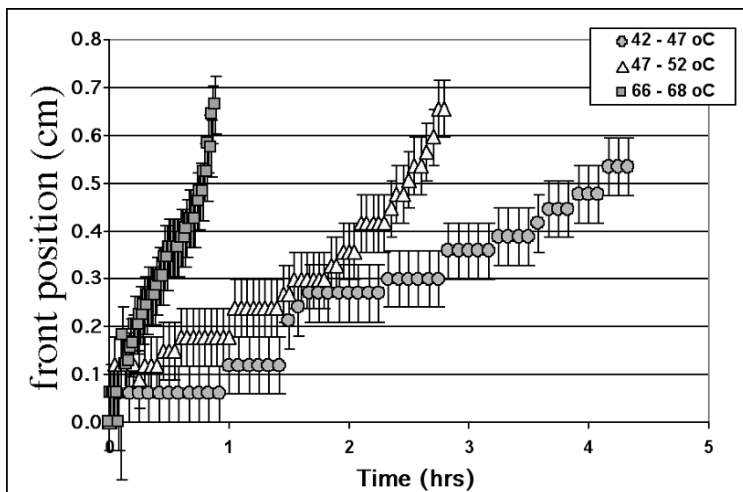*Figure 3.* Mechanism for IFP. The polymerization rate is faster in the high viscosity region.

Figure 4. Propagation of IFP front as a function of time, for three different temperatures. (Adapted from [59].)

Photofrontal polymerization is process driven by the continuous influx of radiation. Typical systems involve a photoinitiator that absorbs the photons and dissociates into free radicals that initiate polymerization. If the dissociation products continue to absorb radiation, then the front position depends logarithmically on time [61]. If the initiator is photobleached, then the front position depends linearly on time [62–66].

4.2. THERMAL FRONTAL POLYMERIZATION

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 [67]. They studied methyl methacrylate polymerization to determine the effect of initiator type and concentration on front velocity [68] and the effect of pressure [69]. The literature up to 1984 was reviewed by Davtyan et al. [70].

4.2.1. *Basic phenomena*

Frontal polymerization reactions are relatively easy to perform. In the simplest case, a test tube is filled with the reactants. The front is ignited by applying heat to one end of the tube with an electric heater. Fronts with free-radical polymerization propagate with velocities from 1 to 20 cm/min. The position of the front is obvious because of the difference in the optical properties of polymer and monomer (Figure 5).
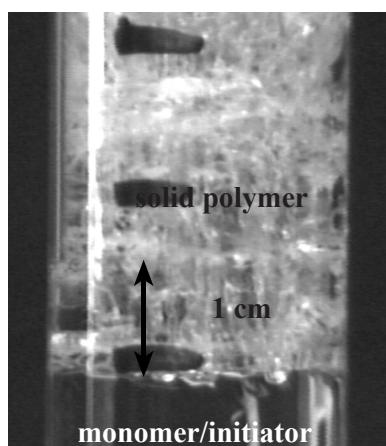

Figure 5. A descending case of frontal polymerization with triethylene glycol dimethacrylate and benzoyl peroxide as the initiator.
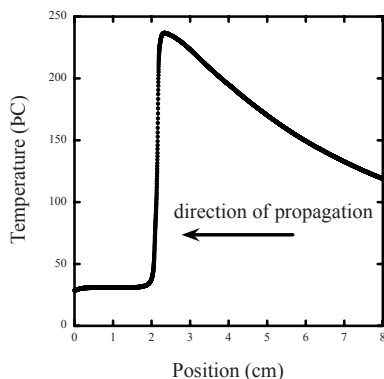
Figure 6. A typical temperature profile for a free-radical polymerization front.

The defining feature of frontal polymerization is the sharp temperature gradient present in the front. Figure 6 shows a typical temperature profile for a thiolene polymerization front [71]. Notice that the temperature jumps about 200°C over as little as a few millimeters, which corresponds to polymerization in a few seconds at that point. For multifunctional acrylates, such as trimethylolpropane triacrylate (TMPTA), maximum front temperature should exceed 400°C, if the reaction proceeded to 100% conversion. One factor that can limit conversion is the equilibrium dependence on temperature [72] and the other is the inherent low conversion obtained with multifunctional acrylates caused by the crosslinking.

4.2.2. *What systems can be performed frontally?*

The requirements for frontal polymerization are a system that does not react at the chosen initial temperature, but does react rapidly at an elevated temperature. The reaction must be exothermic.

An overwhelming majority of work has been on free-radical systems [73] with acrylates and methacrylates [74–76] because of the high reactivities of these monomers. Nason et al. studied the UV-ignited frontal polymerization of acrylates and methacrylates [77] Other free-radical systems can be used such as unsaturated polyester resins [78], and thiol-enes [71], Jiménez and Pojman studied frontal polymerization with polymerizable ionic liquid monomers [79].

Begishev et al. studied frontal anionic polymerization of ε-caprolactam [80,81] and epoxy chemistry has been used as well [82–88]. Mariani et al. demonstrated Frontal Ring-Opening Metathesis Polymerization [89] and Fiori et al. produced polyacrylate/poly(dicyclopentadiene) networks frontally [90]. Polyurethanes have been prepared frontally [91–93]. Frontal atom transfer radical polymerization (ATRP) has been achieved [94].

Photo-activated and induced epoxy systems have been cured frontally. Oxetanes and oxiranes via photoinduced cationic ring opening [95]. Mariani et al. developed an epoxy system in which UV light reacted with a cationic photoinitiator to start the frontal curing of an epoxy. The front propagated through the thermal-induced decomposition of benzoyl peroxide. The radicals produced reacted with the cationic photoinitiator to generate cations to initiate polymerization [88].

Solid monomers can be used if their melting point is sufficiently low [96,97].

Chen et al. reported on segmented polyurethane and polyurethane-nanosilica hybrid nanocomposites synthesized by frontal polymerization [93,98,99]. Chen et al. prepared epoxy resin/polyurethane hybrid networks [99] and urethane–acrylate copolymers [93,100].

A complete bibliography can be found at: http://www.pojman.com/ FP_Bibliography.html.

4.2.3. *Applications*

1. Rapid curing of thick epoxy composites without an autoclave. White has shown it is possible to have a frontal curing of thick layers of a commercial epoxy prepreg with superior properties compared to homogeneous curing [84,87]. Chekanov et al. has shown that standard epoxy/ amine systems can be cured an order of magnitude faster than batch methods while still achieving 90% of the mechanical properties [85].
2. Chekanov and Pojman demonstrated that functionally-gradient materials could be prepared with FP [101]. McCardle and Pojman patented the approach [102,103].
3. Special polymers: Steinbock and Washington prepared temperature-sensitive hydrogels [104]. Microporous polymers have been produced [105,106]. Bidali et al. demonstrated that frontal ATRP of a dimethacrylate resulted in a product with higher conversion and higher degradation temperatures [94].
4. Mariani has reported using FP to consolidate porous stone materials and wood [107–109].
5. HILTI Entwicklung Elektrowerkzeuge GmbH holds a patent on using FP for chemical anchors in which a "mortar" is injected into a hole surrounding a tie bar [110]. FP is initiated to rapidly cure and secure the tie bar.

### 4.2.4. *Free-radical polymerization kinetics*

A free-radical polymerization with a thermal initiator can be approximately represented by a three-step mechanism. First, an unstable compound, usually a peroxide or nitrile, decomposes to produce radicals:

$$I \rightarrow f2R\bullet$$
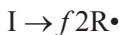
where f is the efficiency, which depends on the initiator type and the solvent. A radical can then add to a monomer to initiate a growing polymer chain:

$$R\bullet + M \rightarrow P_1 \bullet$$
$$P_n\bullet + M \rightarrow P_{n+1}* \qquad\qquad (P)$$

The propagation step (P) continues until a chain terminates by reacting with another chain (or with an initiator radical):

$$P_n\bullet + P_m\bullet \rightarrow P_n + P_m \text{ (or } P_{n+m})$$
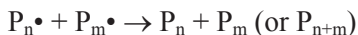
The major heat release in the polymerization reaction occurs in the propagation step. Frontal polymerization autocatalysis takes place through the initiator decomposition step because the initiator radical concentration is the main control for the total polymerization rate.

The rate of polymerization is given by:

$$\frac{d[M]}{dt} = \sqrt{\frac{fk_d[Initiator]}{k_t}}k_p[M]$$

This expression is only valid for low conversion at constant temperature because as the viscosity increases, the termination constant decreases. Typical values for the propagation constant of acrylates are on the order of 10^{-4} $M^{-1}s^{-1}$ but termination constants are on the order of 10^{-7} M^{-1} s^{-1}. An increase in viscosity decreases k_t more than k_p, which results in an overall increase in the rate of polymerization. If the viscosity is too high, then the rate of polymerization can be decreased [111].

Now we can understand an interesting phenomenon for frontal polymerization of acrylates. For a monoacrylate such as butyl acrylate, the front velocity is about 1 cm min^{-1}. Fronts with a diacrylate will be ten times faster. The propagation rate constant is about the same for monoacrylates and multifunctional acrylates but the termination constants are very different. At very low conversion, the polymerization occurs in a crosslinked gel in which termination can not occur. The polymerization rate is thus very high. Figure 7 shows the conversion versus time for both a diacrylate and a monoacrylate. Notice that the diacrylate polymerizes much faster.

This extreme gel effect has two other consequences. Conversion is often much lower for the multifunctional acrylates. Secondly, as the termination rate decreases, its contribution to the overall energy of activation is reduced. The steady-state assumption in the polymerization model gives an approximate relationship between the effective activation energy of the entire polymerization process and activation energy of the initiator decomposition reaction:

$$E_{eff} = E_p + (E_i/2) - (E_t/2)$$

where E_p is the activation energy of the propagation step, E_i is for the initiator decomposition and E_t is that for the termination step. Figure 7 shows the measured energy of activation for photopolymerization of a diacrylate and a triacrylate. The energy of activation for the photoinitiator step is zero so what was measured was $E_p – E_t/2$. Obviously, the energy activation is a strong function of conversion.
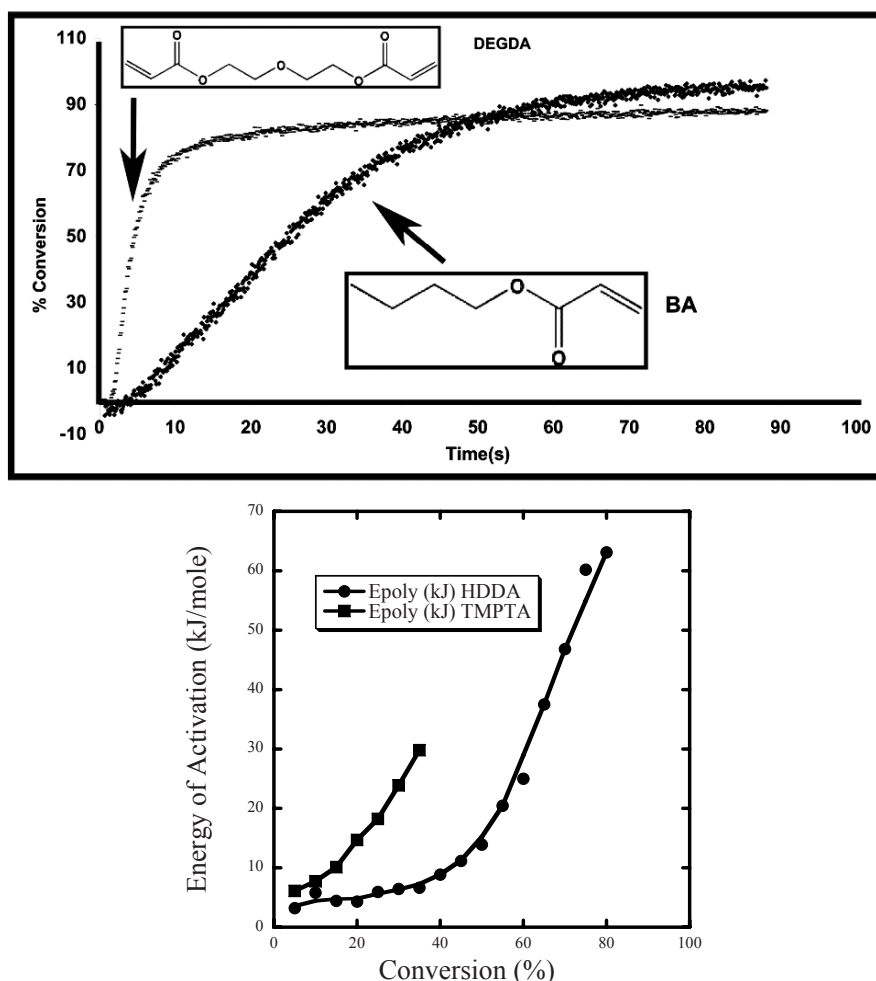

Figure 7. *Top*: Comparison of the conversion as a function of time for the photopolymerization of a diacrylate and a monoacrylate. (Image courtesy of Zulma Jiménez.) *Bottom:* Comparison of the energy of activation as a function of conversion for a 1,6 hexanedioldiacrylate (HDDA) and trimethylol propane triacrylate (TMPTA). (Adapted from [115].)

4.3. CONVECTIVE INSTABILITIES

Because of the large thermal and concentration gradients, polymerization fronts are highly susceptible to buoyancy-induced convection. Pojman et al. reviewed the work [112]. I wish to emphasize two points: First, FP systems demonstrated that chemical reactions must be taken into account when determining the stability conditions, that is, the front does not create density gradients and the fluid responds. The front velocity become another para-meter in determining the critical conditions [113,114].

The second point is that convection can have practical significance. For FP producing a solid front from a low viscosity monomer, the front needs to descend the tube. However, liquid/liquid systems are more complicated because a descending front can exhibit the Rayleigh-Taylor instability. The product is hotter than the reactant but is more dense, and because the product is a liquid, fingering can occur. Such front degeneration is shown in Figure 8. The Rayleigh-Taylor instability can be overcome by increasing the viscosity with addition of a filler.
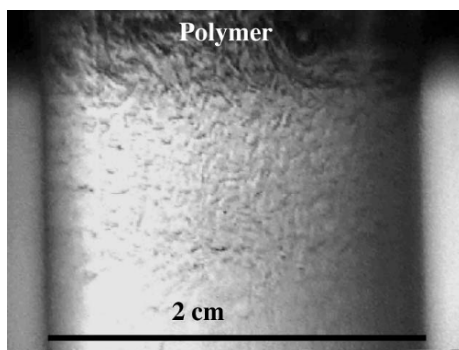

Figure 8. Rayleigh-Taylor instability with a descending front of butyl acrylate polymerization.

4.4. THERMAL INSTABILITIES

Fronts do not have to propagate as planar fronts. Analogously to oscillating reactions, a steady state can lose its stability as a parameter is varied and exhibit periodic behavior, either as pulsations or "spin modes" in which a hot spot propagates around the reactor as the front propagates, leaving a helical pattern.

The linear stability analysis of the longitudinally propagating fronts in the cylindrical adiabatic reactors with one overall reaction predicted that the expected frontal mode for the given reactive medium and diameter of reactor is governed by the Zeldovich number:

$$Z = \frac{T_\mathrm{m} - T_o}{T_m} \frac{E_{\mathit{eff}}}{RT_m}$$

For FP, lowering the initial temperature (T_0), increasing the front temperature (T_m), increasing the energy of activation (E_{eff}) all increase the Zeldovich number. The planar mode is stable if $Z < Z_{cr} = 8.4$, and unstable if $Z > Z_{cr}$. The most commonly observed case with frontal polymerization is the spin mode in which a "hot spot" propagates around the front. A helical pattern is often observed in the sample (Figure 9). The first case was with the frontal polymerization of ε-caprolactam [80,81], and the next case was discovered by Pojman et al. in the methacrylic acid system in which the initial temperature was lowered [116].

At room temperature, multifunctional acrylates exhibit spin modes although monoacrylates do not. In fact, if an inert diluent, such as dimethyl sulfoxide (DMSO) is added, the spins modes are more apparent even though the front temperature is reduced [117]. We can understand this from Figure 7 in which the contribution to the energy activation from the polymerization kinetics depends on conversion and is always much higher than for a monoacrylate. Masere et al. found that changing the ratio of a mono-acrylate to a diacrylate, keeping the front temperature constant, would cause a variety of spin modes. Changing the ratio of the acrylates changed the effective energy of activation for the front.

FP allows the study of spherically propagating fronts. Binici et al. developed a system that was a gel created by the base-catalyzed reaction of a trithiol with a triacrylate [118]. The system could still support a thermal front because of unreacted acrylate and the presence of a dissolved peroxide (Figure 10).
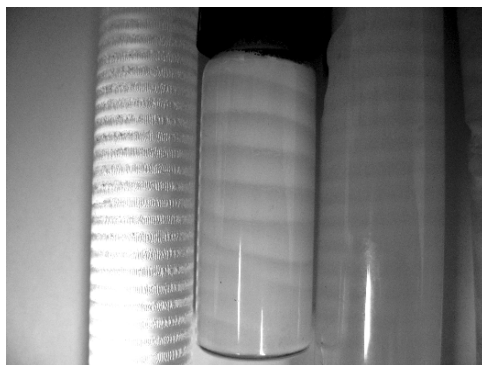

Figure 9. Helical patterns produced by "spin modes" in three different frontal polymerization systems. Tube diameters are approximately 1.5 cm.
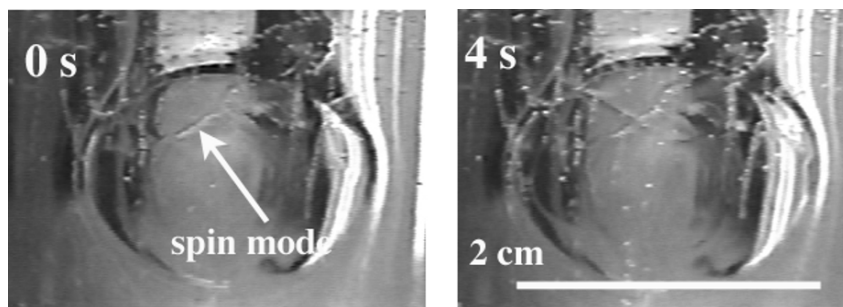
Figure 10. A spin mode on the surface of a spherically-expanding front of triacrylate polymerization.

5. Conclusions

Synthetic polymer systems can be created that exhibit a variety of interesting dynamical behavior. This can be achieved by coupling a polymerization to another dynamical system or by exploiting intrinsic nonlinearities of some polymerizations. Both methods have their virtues but not enough work has been done on identifying feedback mechanisms in polymerizations. Focusing on these feedback mechanisms and applying the experiences from inorganic systems, should lead to the development of new and useful systems.

References

1.   G. Odian, *Principles of Polymerization*, 4th Ed. (Wiley, New York, 2004).
2.   H. R. Allcock and F. W. Lampe, *Contemporary Polymer Chemistry* (Prentice-Hall, Englewood Cliffs, NJ, 1981).
3.   L. H. Sperling, *Introduction to Physical Polymer Science* (Wiley, New York, 1992).
4.   A. Goldbeter, *Biochemical Oscillations and Cellular Rhythms: The Molecular Bases of Periodic and Chaotic Behaviour* (Cambridge University Press, Cambridge, UK, 1996).
5.   I. R. Epstein and J. A. Pojman, *An Introduction to Nonlinear Chemical Dynamics: Oscillations, Waves, Patterns and Chaos* (Oxford University Press, New York, 1998).
6.   R. G. W. Norrish and R. R. Smith, *Nature* **150**, 336–337 (1942).
7.   E. Trommsdorff, H. Köhle and P. Lagally, *Makromol. Chem*. **1**, 169–198 (1948).
8.   G. O. O'Neal, M. B. Wusnidel and J. M. Torkelson, *Macromolecules* **31**, 4537–4545 (1998).
9.   G. O. O'Neal, M. B. Wusnidel and J. M. Torkelson, *Macromolecules* **29**, 7477–7490 (1996).
10.   R. L. Kaas, *J. Polym. Sci. Polym. Chem. Ed.* **19**, 2255–2267 (1981).
11.   J. Mijovic and J. Wijaya, *Macromolecules* **27**, 7589–7600 (1994).

12. I. P. Aspin, J. M. Barton, G. J. Buist, A. S. Deazle and I. Hammerton, *J. Mater. Chem.* **4**, 385–388 (1994).

13. J. P. Eloundou, M. Feve, D. Harran and J. P. Pascault, *Die Ang. Makrom. Chem.* **230**, 13–46 (1995).

14. S. Mu and J. Kan, *Electrochim. Acta* **41**, 1593–1599 (1996).

15. R. Mazeikiene and A. Malinauskas, *Synthetic Metals* **108**, 9–14 (2000).

16. C. Karunakaran and P. N. Palanisamy, *J. Mol. Catal. A Chem.* **172**, 9–17 (2001).

17. T. Tanaka, *Phys. Rev. Lett.* **40**, 820–823 (1978).

18. J. P. C. Addad, *Physical Properties of Polymer Gels* (Wiley, Chichester, U.K., 1996).

19. S. Hirotsu, Y. Hirokawa and T. Tanaka, *J. Chem. Phys.* **87**, 1392–1395 (1987).

20. Q. Tran-Cong and A. Harada, *Phys. Rev. Lett.* **76**, 1162–1165 (1996).

21. Q. Tran-Cong, A. Harada, K. Kataoka, T. Ohta and O. Urakawa, *Phys. Rev. E* **55**, R6340–R6343 (1997).

22. V. Edel, *Macromolecules* **28**, 6219–6228 (1995).

23. G. P. Andrianova, A. S. Kechkyan and V. A. Kargin, *J. Poly. Sci.* **9**, 1919–1933 (1971).

24. J. Crank, *Mathematics of Diffusion* (Clarendon Press, Oxford, 1975).

25. F. V. Burkersroda, L. Schedl and A. G. Opferich, *Biomaterials* **23**, 4221–4231 (2002).

26. E. T. Severs, *Rheology of Polymers* (Reinhold, New York, 1962).

27. J. D. Ferry, *Viscoelastic Properties of Polymers* (Wiley, New York, 1980).

28. R. K. Gupta, *Polymer and Composite Rheology* (Marcel Dekker, New York, 2000).

29. J. Meissner, *J. Appl. Polym. Sci.* **16**, 2877–2899 (1972).

30. R. B. Bird, R. C. Armstrong and O. Hassager, *Dynamics of Polymeric Liquids*, Vol. 1, 2nd Ed. (Wiley, New York, 1987).

31. J. A. Pojman, A. L. Garcia, D. K. Kondepudi and C. Van den Broeck, *J. Phys. Chem.* **95**, 5655–5660 (1991).

32. Z. Váradi and M. T. Beck, *J. Chem. Soc. Chem. Commun.* 30–31 (1973).

33. J. A. Pojman, D. C. Leard and W. West, *J. Am. Chem. Soc.* **114**, 8298–8299 (1992).

34. R. P. Washington, G. P. Misra, W. W. West and J. A. Pojman, *J. Am. Chem. Soc.* **121**, 7373–7380 (1999).

35. R. Yoshida, H. Ichijo, T. Hakuta and T. Yamaguchi, *Macromol. Rapid Commun.* **16**, 305–310 (1995).

36. R. Yoshida, S. Onodera, T. Yamaguchi and E. Kokufuta, *J. Phys. Chem. A* **103**, 8573–8578 (1999).

37. Y. Hara and R. Yoshida, *Langmuir* **21**, 9773–9776 (2005).

38. V. V. Yashin and A. C. Balazs, *Macromolecules* **39**, 2024–2026 (2006).

39. V. V. Yashin and A. C. Balazs, *Science* **314**, 798–800 (2006).

40. M. Li, S. Xu and E. Kumacheva, *Macromolecules* **33**, 4972–4978 (2000).

41. Z. Mitov and E. Kumacheva, *Phys. Rev. Lett.* **81**, 3427–3430 (1998).

42. O. Karthaus, K. Kaga, J. Sato, S. Kurimura, K. Okamoto and T. Imai, in *Nonlinear Dynamics in Polymeric Systems*, ACS Symposium Series No. 869, edited by J. A. Pojman and Q. Tran-Cong-Miyata (American Chemical Society, Washington, DC, 2003), pp. 199–211.

43. J. Boissonade, *Phys. Rev. Lett.* **90**, 188302 (2003).

44. F. Gauffre, V. Labrot, J. Boissonade and P. De Kepper, in *Nonlinear Dynamics in Polymeric Systems*, ACS Symposium Series No. 869, edited by J. A. Pojman and Q. Tran-Cong-Miyata (American Chemical Society, Washington, DC, 2003), pp. 80–93.

45. V. Labrot, P. De Kepper, J. Boissonade, I. Szalai and F. Gauffre, *J. Phys. Chem. B* **109**, 21476–21480 (2005).

46. J. Boissonade, *Chaos* **15**, 023703 (2005).

47. A. P. Dhanarajan, G. P. Misra and R. A. Siegel, *J. Phys. Chem. A* **106**, 8835–8838 (2002).

48. J.-C. Leroux and R. A. Siegel, *Chaos* **9**, 267–275 (1999).

49. T. R. Keane, in *Chemical Reaction Engineering: Proceedings of the Fifth European/Second International Symposium on Chemical Reaction Engineering*, edited by J. M. H. Fortuin (Elsevier, Amsterdam, 1972), pp. A7-1–A7-9.

50. F. Teymour and W. H. Ray, *Chem. Eng. Sci.* **47**, 4121–4132 (1992).

51. F. Teymour and W. H. Ray, *Chem. Eng. Sci.* **47**, 4133–4140 (1992).

52. G. Papavasiliou and G. Teymour, in *Nonlinear Dynamics in Polymeric Systems*, ACS Symposium Series No. 869, edited by J. A. Pojman and Q. Tran-Cong-Miyata (American Chemical Society, Washington, DC, 2003), pp. 309–323.

53. F. J. Schork and W. H. Ray, *J. Appl. Poly. Sci.* (*Chem.*) **34**, 1259–1276 (1987).

54. A. Harada and Q. Tran-Cong, *Macromolecules* **30**, 1643–1650 (1997).

55. Q. Tran-Cong-Miyata, S. Nishigami, S. Yoshida, T. Ito, K. Ejiri and T. Norisuye, in *Nonlinear Dynamics in Polymeric Systems*, ACS Symposium Series No. 869, edited by J. A. Pojman and Q. Tran-Cong-Miyata (American Chemical Society, Washington, DC, 2003), pp. 276–291.

56. Y. Koike, Y. Takezawa and Y. Ohtsuka, *Appl. Opt.* **27**, 486–491 (1988).

57. B. R. Smirnov, S. S. Min'ko, I. A. Lusinov, A. A. Sidorenko, E. V. Stegno and V. V. Ivanov, *Vysokomol. Soedin., Ser. B* **35**, 161–162 (1993).

58. L. L. Lewis, C. A. DeBisschop, J. A. Pojman and V. A. Volpert, in *Nonlinear Dynamics in Polymeric Systems*, ACS Symposium Series No. 869, edited by J. A. Pojman and Q. Tran-Cong-Miyata (American Chemical Society, Washington, DC, 2003), pp. 169–185.

59. L. L. Lewis, C. S. DeBisschop, J. A. Pojman and V. A. Volpert, *J. Polym. Sci. A Polym. Chem.* **43**, 5774–5786 (2005).

60. S. I. Evstratova, D. Antrim, C. Fillingane and J. A. Pojman, *J. Polym. Sci. A Polym. Chem.* **44**, 3601–3608 (2006).

61. V. A. Briskman, in *Polymer Research in Microgravity: Polymerization and Processing*, ACS Symposium Series No. 793, edited by J. P. Downey and J. A. Pojman (American Chemical Society, Washington, DC, 2001), pp. 97–110.

62. V. Narayan and A. B. Scranton, *Trends Polym. Sci.* (*Camb.*) **5**, 415–419 (1997).

63. L. S. Coons, B. Rangarajan, D. Godshall and A. B. Scranton, in *Photopolymerization: Fundamentals and Applications*, ACS Symposium Series 673, edited by A. B. Scranton, C. N. Bowman and R. W. Peiffer (American Chemical Society, Washington, DC, 1997) pp. 203–218.

64. G. A. Miller, L. Gou, V. Narayanan and A. B. Scranton, *J. Poly. Sci. A Polym. Chem.* **40**, 793–808 (2002).

65. J. T. Cabral, S. D. Hudson, C. Harrison and J. F. Douglas, *Langmuir* **20**, 10020–10029 (2004).

66. J. A. Warren, J. T. Cabral and J. F. Douglas, *Phys. Rev. E* **72**, 021801 (2005).

67. N. M. Chechilo, R. J. Khvilivitskii and N. S. Enikolopyan, *Dokl. Akad. Nauk SSSR* **204**, 1180–1181 (1972).

68. N. M. Chechilo and N. S. Enikolopyan, *Dokl. Phys. Chem.* **221**, 392–394 (1975).

69. N. M. Chechilo and N. S. Enikolopyan, *Dokl. Phys. Chem.* **230**, 840–843 (1976).

70. S. P. Davtyan, P. V. Zhirkov and S. A. Vol'fson, *Russ. Chem. Rev.* **53**, 150–163 (1984).

71. J. A. Pojman, B. Varisli, A. Perryman, C. Edwards and C. Hoyle, *Macromolecules* **37**, 691–693 (2004).

72. J. A. Pojman, V. M. Ilyashenko and A. M. Khan, *J. Chem. Soc. Faraday Trans.* **92**, 2825–2837 (1996).

73. R. P. Washington and O. Steinbock, *Polym. News* **28**, 303–310 (2003).

74. J. A. Pojman, *J. Am. Chem. Soc.* **113**, 6284–6286 (1991).
75. J. A. Pojman, J. R. Willis, A. M. Khan and W. W. West, *J. Polym. Sci. A Polym. Chem.* **34**, 991–995 (1996).
76. P. M. Goldfeder, V. A. Volpert, V. M. Ilyashenko, A. M. Khan, J. A. Pojman and S. E. Solovyov, *J. Phys. Chem. B* **101**, 3474–3482 (1997).
77. C. Nason, T. Roper, C. Hoyle and J. A. Pojman, *Macromolecules* **38**, 5506–5512 (2005).
78. S. Vicini, A. Mariani, E. Princi, S. Bidali, S. Pincin, S. Fiori, E. Pedemonte, and A. Brunetti, *Polym. Adv. Technol.* **16**, 293–298, (2005).
79. Z. Jiménez and J. A. Pojman, *J. Polym. Sci. A Polym. Chem.* **45**, 2745–2754 (2007).
80. V. P. Begishev, V. A. Volpert, S. P. Davtyan and A. Y. Malkin, *Dokl. Akad. Nauk SSSR* **208**, 892 (1973).
81. V. P. Begishev, V. A. Volpert, S. P. Davtyan and A. Y. Malkin, *Dokl. Phys. Chem.* **279**, 1075–1077 (1985).
82. S. P. Davtyan, K. A. Arutyunyan, K. G. Shkadinskii, B. A. Rozenberg and N. S. Yenikolopyan, *Polymer Science U.S.S.R.* **19**, 3149–3154 (1978).
83. V. N. Korotkov, Y. A. Chekanov and B. A. Rozenberg, *Comp. Sci. & Tech.* **47**, 383–388 (1993).
84. S. R. White and C. Kim, *J. Reinforced Plastics and Comp.* **12**, 520–535 (1993).
85. Y. Chekanov, D. Arrington, G. Brust and J. A. Pojman, *J. Appl. Polym. Sci.* **66**, 1209–1216 (1997).
86. S. R. White and C. Kim, in *Thermochemical Modeling of an Economical Manufacturing Technique for Composite Structures*, 37th International SAMPE Symposium Exhibition (Long Beach, California, 1992), pp. 240–251.
87. C. Kim, H. Teng, C. L. Tucker and S. R. White, *J. Comp. Mater.* **29**, 1222–1253 (1995).
88. A. Mariani, S. Bidali, S. Fiori, M. Sangermano, G. Malucelli, R. Bongiovanni and A. Priola, *J. Poly. Sci. Part A: Polym. Chem.* **42**, 2066–2072 (2004).
89. A. Mariani, S. Fiori, Y. Chekanov and J. A. Pojman, *Macromolecules* **34**, 6539–6541 (2001).
90. S. Fiori, A. Mariani, L. Ricco and S. Russo, *e-Polymers* **29**, 1–10 (2002).
91. S. Fiori, A. Mariani, L. Ricco and S. Russo, *Macromolecules* **36**, 2674–2679 (2003).
92. A. Mariani, S. Bidali, S. Fiori, G. Malucelli and E. Sanna, *e-Polymers* **44**, 1–9 (2003).
93. S. H. Chen, J. Sui and L. Chen, *Colloid and Polymer Science* **283**, 932–936 (2005).
94. S. Bidali, S. Fiori, G. Malucelli and A. Mariani, *e-Polymers* **60**, 1–12 (2003).
95. J. V. Crivello, *J. Polym. Sci. Part A: Polym. Chem.* **45**, 4331–4340 (2007).
96. J. A. Pojman, I. P. Nagy and C. Salter, *J. Am. Chem. Soc.* **115**, 11044–11045 (1993).
97. D. I. Fortenberry and J. A. Pojman, *J. Polym. Sci. Part A: Polym. Chem.* **38**, 1129–1135 (2000).
98. S. Chen, J. Sui, L. Chen and J. A. Pojman, *J. Polym. Sci. Part A: Polym. Chem.* **43**, 1670–1680 (2005).
99. S. Chen, Y. Tian, L. Chen and T. Hu, *Chem. Mater.* **18**, 2159–2163 (2006).
100. T. Hu, S. Chen, Y. Tian, J. A. Pojman and L. Chen, *J. Poly. Sci. Part A: Polym. Chem.* **44**, 3018–3024 (2006).
101. Y. A. Chekanov and J. A. Pojman, *J. Appl. Polym. Sci.* **78**, 2398–2404 (2000).
102. J. A. Pojman and T. W. McCardle, Functionally gradient polymeric materials, U.S. Patent, 6,057,406 (2000).
103. J. A. Pojman and T. W. McCardle, Functionally gradient polymeric materials, U.S. Patent, 6,313,237 (2001).
104. R. P. Washington and O. Steinbock, *J. Am. Chem. Soc.* **123**, 7933–7934 (2001).

105. N. S. Pujari, A. R. Vishwakarma, M. K. Kelkar and S. Ponrathnam, *e-Polymers* **49**, 1–10 (2004).

106. N. S. Pujari, A. R. Vishwakarma, T. S. Pathak, A. M. Kotha and S. Ponrathnam, *Bulletin of Materials Science* **27**, 529–536 (2004).

107. S. Vicini, A. Mariani, E. Princi, S. Bidali, S. Pincin, S. Fiori, E. Pedemonte and A. Brunetti, *Polym. Adv. Technol.* **16**, 293–298 (2005).

108. A. Mariani, S. Bidali, P. Cappelletti, G. Caria and A. Colella, *e-Polymers* (2006).

109. A. Brunetti, A. Mariani and S. Bidali, *Nuovo Cimento- Societa Italiana di Fisica Sezione C* **30**, 407–416 (2007).

110. A. Pfeil, T. Burgel, M. Morbidelli and A. Rosell, Mortar composition, curable by frontal polymerization, and a method for fastening tie bars, U.S. Patent, 6,533,503 (2003).

111. H. Zhou, Z. Jiménez, J. A. Pojman, M. S. Paley and C. E. Hoyle, *J. Polym. Sci. A: Polym. Chem.* **46**, 3766–3773 (2008).

112. J. A. Pojman, S. Popwell, D. I. Fortenberry, V. A. Volpert and V. A. Volpert, in *Nonlinear Dynamics in Polymeric Systems*, ACS Symposium Series No. 869, edited by J. A. Pojman and Q. Tran-Cong-Miyata (American Chemical Society, Washington, DC, 2003), pp. 106–120.

113. G. Bowden, M. Garbey, V. M. Ilyashenko, J. A. Pojman, S. Solovyov, A. Taik and V. Volpert, *J. Phys. Chem. B* **101**, 678–686 (1997).

114. B. McCaughey, J. A. Pojman, C. Simmons and V. A. Volpert, *Chaos* **8**, 520–529 (1998).

115. K. N. Gray, *Photopolymerization Kinetics of Multifunctional Acrylates* (University of Southern Mississippi, Hattiesburg, MS, 1988).

116. J. A. Pojman, V. M. Ilyashenko and A. M. Khan, *Physica D* **84**, 260–268 (1995).

117. J. Masere and J. A. Pojman, *J. Chem. Soc. Faraday Trans.* **94**, 919–922 (1998).

118. B. Binici, D. I. Fortenberry, K. C. Leard, M. Molden, N. Olten, S. Popwell and J. A. Pojman, *J. Polym. Sci. A Polym. Chem.* **44**, 1387–1395 (2006).