

6-1-1999

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Masere, J., Stewart, F., Meehan, T., Pojman, J. A. (1999). Period-Doubling Behavior in Frontal Polymerization of Multifunctional Acrylates. *Chaos*, 9(2), 315-322.
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Period-doubling behavior in frontal polymerization of multifunctional acrylates

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(Received 5 June 1998; accepted for publication 5 December 1998)

Front dynamics in the frontal polymerization of two multifunctional acrylate monomers, 1,6-hexanediol diacrylate (HDDA) and trimethylolpropane ethoxylate triacrylate (TMPTA), with Lupersol 231 [1,1-di(*t*-butylperoxy)-3,3,5-trimethylcyclohexane] as the initiator, are studied. In most frontal polymerization systems, the dynamics are associated with a planar front propagating through the sample. However, in some cases, front behavior can be altered: the front becomes nonplanar characterized by complex patterns like spin modes and pulsations. To determine how these periodic and aperiodic modes arise, reactant solutions consisting of HDDA diluted with diethyl phthalate (DEP) and TMPTA diluted with dimethyl sulfoxide (DMSO) were used in the study. In the study we reveal frontal behavior characteristic of period-doubling behavior, a doubling of spin heads that degenerate into an apparently chaotic mode. Also, a pulsating symmetric mode has been observed. These observations have a striking similarity to observations made in studies of self-propagating high-temperature synthesis (SHS) in which the addition of an inert diluent afforded a rich variety of dynamical behavior. The degree of cross-linking has also been found to be a bifurcation parameter. The energy of activation of multifunctional acrylate polymerization is a strong function of the degree of polymerization. By adding a monoacrylate (benzyl acrylate: BzAc), such that the front temperature was invariant, we observed a period-doubling bifurcation sequence through changes in the energy of activation, which has not been previously reported. © 1999 American Institute of Physics. [S1054-1500(99)01202-1]

In frontal polymerization, a method of producing polymeric materials via a thermal front that propagates through the unreacted monomer/initiator solution, periodic modes can arise when a parameter, the Zeldovich number, is varied. We have explained that multifunctional acrylates exhibit periodic modes at room temperature because the energy of activation is much higher when cross-linking occurs. Using an inert diluent, we found a period-doubling bifurcation sequence in the number of spinning “hot spots” and observed for the first time pulsating symmetric modes. We have shown that the degree of cross-linking can also serve as a bifurcation parameter, controlled through the addition of a reactive diluent that is monofunctional acrylate.

I. INTRODUCTION

Self-propagating high-temperature synthesis (SHS), a process in which the heat released by the reaction is utilized to sustain the synthesis, has proven to be simple and cost effective in terms of energy consumption and time.^{1–8} Reactants are placed in a cylinder, and when the reaction is initiated at one end, a self-sustaining reaction propagates through the sample. In addition to low-energy costs, this approach is advantageous in that metastable materials can be formed that would otherwise be unattainable by a homogeneous process.

Since the development of SHS by Merzhanov and co-workers,⁹ an increasing research effort has been invested in the field and a whole range of products have been synthesized. In the majority of SHS materials processing, a planar uniform reaction front propagating at a constant velocity is observed. Changes in the system, such as heat loss or initial composition, can cause the planar mode to lose its stability. Several different modes may appear, namely, pulsating fronts and spin modes. Pulsating fronts travel with an oscillatory velocity but the fronts remain flat. Spin modes are characterized by a nonplanar front with one or more high-temperature regions, “hot spots,” that move in a helical path along the axis of the reaction vessel. Experimental studies have shown such propagation modes in both solid–gas systems^{5,6,10} and solid–solid systems.¹¹ These studies have shown that low gaseous reactant pressure, low densities of reactant mixtures, and excessive dilution of the system are among the conditions that culminate in such instabilities.

These front dynamics have also been studied numerically and analytically.^{12–14} Novozhilov presented a review of these aspects in 1992.¹⁵ Analytical studies have shown that changes in the reaction activation energy can result in nonplanar fronts.¹⁶ Theoretical studies have also shown that models assuming melting or nonmelting of a solid reactant differ in the various transitions describing the passage between stable and unstable modes, typical of a period-doubling route to chaotic propagation.¹⁷ Shkuro *et al.* demonstrated a period doubling in the propagation of tantalum–carbon combustion fronts.¹⁸ Bayliss and Matkowsky¹⁷

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performed a theoretical study in which a system's bifurcation parameter was varied and corresponding qualitative changes in the behavior of the front were predicted. The bifurcation parameter was a function of the activation energy of the one-step reaction, the initial reactant temperature, and the front temperature.

However, experimental studies of SHS systems are difficult because of the high temperatures (above 1000 °C) and the large front velocities associated with thermite reactions.¹ Polymerization fronts are more amenable for experimental studies because they are cooler (200 °C), have slower front velocities and involve inexpensive reagents. Traveling fronts of addition polymerizations are similar to condensed-phase SHS reactions because both involve a purely thermal propagation mechanism. By coupling exothermic free-radical polymerization reactions and thermally unstable compounds that yield free radicals upon heat-induced decomposition, a self-sustaining propagating reaction front can be observed. This is called frontal polymerization, and there is an exhaustive review of this process by Pojman *et al.*¹⁹

There is a rich history of frontal polymerization, particularly from studies done by Chechilo *et al.*^{20–23} Apart from free-radical addition polymerizations, reactions fronts were also found for the curing of epoxy resins.^{24–29} Pojman and co-workers have demonstrated frontal free-radical polymerizations using many high boiling point liquid monomers.^{19,30–32} They have also demonstrated propagating fronts through solid monomers.^{33–35}

However, relatively few experimental investigations have focused specifically on periodic and aperiodic fronts during frontal polymerization. Although spin modes were observed in the anionic polymerization of ϵ -caprolactam^{36,37} and a subsequent stability analysis done by Volpert and Volpert,³⁸ the system has a disadvantage in that the front does not have a constant velocity because of homogeneous polymerization that occurs at the elevated temperatures (350 K) necessary to sustain a front. The first true spin mode for a system with a constant front velocity was reported by Pojman *et al.*³⁹ They showed that at an initial temperature of 0 °C, the frontal methacrylic acid polymerization exhibits spin modes.

A better understanding of these modes has important ramifications if frontal polymerization is to be used for the production of materials at an industrial level. The quality of frontal polymerization products depends on the local microstructure, which, in turn, is related to the temperature history. Nonplanar frontal propagation induces inhomogeneities in the product. Ways to prevent such instabilities can only be formulated if factors responsible are known and well understood. In this paper, we have investigated the frontal polymerization of 1,6-hexanediol diacrylate (HDDA) and trimethylolpropane ethoxylate triacrylate (TMPTA).

II. MODELS OF FRONT INSTABILITIES

Numerical and analytical studies of nonstationary equations describing the thermal reaction propagating fronts in SHS systems have revealed a wealth of dynamical behavior.^{12,17,40,41} The simplest propagation mode is charac-

terized by a planar front with a constant velocity Fig. 1(a). However, in some of the systems studied, the movement of the front actually occurs in nonplanar modes and/or planar pulsating modes. The possible realization of these modes depends on the monomer composition, the amount of inert diluent, the initial temperature of the reactant mixture, heat generation and transfer, and other factors. Theory predicts pulsating and spin modes, both of which have been observed in SHS systems.⁶

An expression that can be used to estimate the boundary between the various modes has been formulated:

$$Z = \frac{E_a}{RT_{\max}} \left(1 - \frac{T_0}{T_{\max}} \right),$$

where T_{\max} is the maximum temperature, T_0 is the initial temperature of the reactant mixture, E_{eff} is the effective activation energy, and R is the gas constant. The theory behind this equation was propounded by Zeldovich and co-workers.^{42–45}

This expression yields qualitative information on how the front regimes depend on the variation of the initial and final temperatures. By changing T_0 , Pojman *et al.*³⁹ observed changes in the frontal behavior in the polymerization of methacrylic acid. Spin modes were observed with changes in heat transfer and the initial temperature.^{19,39,46} Polymerization fronts in 1–2 cm diameter test tubes follow the theories, assuming adiabatic conditions, quite well.⁴⁶

When $Z < 8.4$, the front is in a stationary regime in which the front propagates at a constant velocity, and the reaction occurs in a narrow zone between the reactant mix-

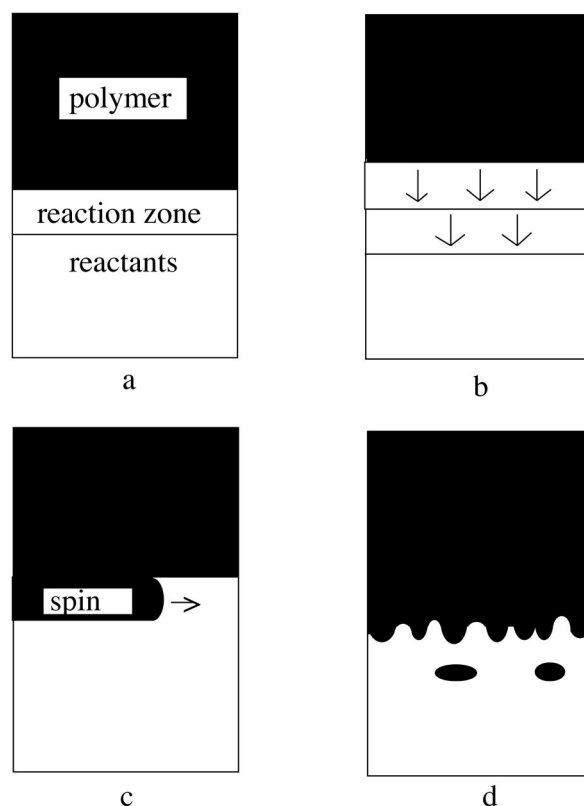


FIG. 1. Modes of frontal propagation.

ture and the product, as shown in Fig. 1(a). That mode becomes unstable when $Z > 8.4$, culminating in a pulsating planar front. A pulsating front is a planar regime in which a front propagates with an oscillatory velocity. Pulsating fronts can either be planar or nonplanar. Figure 1(b) shows an illustration of a planar pulsating front. Although this mode has been observed in SHS,^{4,5,11} it has not been seen in frontal polymerization systems. Ilyashenko and Pojman showed that the conditions for experiments with methacrylic acid were outside the pulsating regime, but they did observe spin modes.⁴⁶ A spinning front, Fig. 1(c), is a propagation mode characterized by a reaction zone moving in a spiral fashion, leaving behind a discernible trace. The ultimate nonplanar regime exhibits a front that has apparently randomly migrating hot spots, Fig. 1(d). Such fronts propagate aperiodically.

For a particular system, these modes can be observed if a parameter related to the system is changed, for example, a change in T_0 . By varying this parameter, a bifurcation sequence of frontal modes is observed. In this paper we present the results of our study in which we investigated the order of appearance of these modes in frontal polymerization reactions.

This study is important in the production of materials by frontal polymerization. In studies with monoacrylates, spin modes never appeared at room temperature. However, Masere and Pojman found spin modes in the frontal polymerization of a diacrylate at an ambient condition.⁴⁷ Thus, although the mechanical quality of the resultant polymer material can be improved by using multifunctional acrylates, spin modes may appear and a nonuniform product results. This observation implicates the role of polymer cross-linking in front dynamics.

Tryson and Schultz studied the energy of activation of photopolymerized multifunctional acrylates and found it increased with increasing conversion because of cross-linking, which affects the propagation and termination steps.⁴⁸ Gray found that the energy of activation of HDDA and TMPTA increased exponentially during the reaction.⁴⁹ Using the steady-state theory of polymerization in tandem with Gray's results,⁴⁹ we can calculate the effective energy of activation for thermally initiated polymerization (photoinitiation has no energy of activation) by including the energy of activation of a typical peroxide. Figure 2 shows how the energy of activation increases from a value of about 80 kJ/mole, the same as methacrylic acid, to much greater values.⁴⁹ This can explain how spin modes appear at room temperature with diacrylates but not monoacrylates. The Zeldovich number of methacrylic acid polymerization at room temperature is 7.2, below the stability threshold. Using activation energies at the highest conversions that can be obtained with HDDA and TMPTA, we estimate Zeldovich numbers of 12 and 9, respectively.

However, we hasten to add that no theory has been developed for the stability of systems in which the energy of activation is a function of conversion. We propose that the dynamics are a function of the energy of activation at the highest degree of conversion, but it is also possible that changing the functional dependence on conversion has a similar effect, and thus plays a role. Clearly, more theoretical

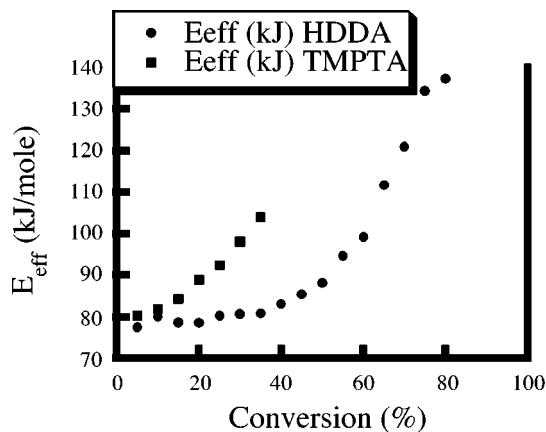


FIG. 2. The dependence of the effective activation energy, E_{eff} on percentage conversion for the thermal polymerization of HDDA and TMPTA, with data from Gray (Ref. 49).

analysis needs to be done, but it will be difficult because the standard infinitely narrow reaction zone hypothesis cannot be invoked.

Because both systems are beyond the stability boundary at room temperature, we decided to add a passive diluent, diethyl phthalate, to lower the front temperature and thus the Zeldovich number. It is noteworthy to point out that the variation of the Zeldovich number with T_{max} depends on T_{max} according to the following equation:

$$\frac{dZ}{d\tau} = \frac{E}{\tau^2} \left(\frac{2}{\tau} - 1 \right),$$

where $E = E_a/RT_0$ and $\tau = T_{\text{max}}/T_0$. As long as $\tau > 2$, a decrease in T_{max} results in an increase in Z . However, when $\tau < 2$, a decrease in T_{max} decreases Z . The former criterion is true for combustion synthesis and the latter is generally true for this study. The use of a passive diluent like diethyl phthalate as a plasticizer also lowers Z by decreasing the effective energy of activation. Due to an increase in the polymer-free volume, the effective degree of cross-linking is lowered, and there is a subsequent decrease in the effective activation energy according to Fig. 2. Using a reactive diluent, benzyl acrylate, a monofunctional acrylate to decrease the degree of cross-linking while maintaining T_{max} constant we, for the first time, introduce a method in which the energy of activation of a reaction is used as a bifurcation parameter.

III. EXPERIMENTAL PROCEDURE

The following reagents, DMSO, HDDA, TMPTA, and DEP, were all purchased from Aldrich and used as received. Benzyl acrylate from DAJAC was also used without further purification. Lupersol 231, used as an initiator, was obtained from ATOCHEM and used without further purification.

For the study of the effects of reactive diluents on front behavior, an arbitrary change in the volume of HDDA was made and the corresponding volumes of BzAc that would result in a constant vinyl concentration, were computed. The vinyl concentration was maintained at 0.11 M. The volume of Lupersol was kept constant at 1.0 mL, and DEP was used to adjust the total volume to 25.0 mL.

TABLE I. Effect of passive diluent on HDDA fronts.

% HDDA	% DEP	Front behavior
38–42	62–58	1 head
42–46	38–34	2 heads
46–49	54–51	4 heads
>49	<51	Fast and flat fronts

A solution of the reactant mixture was placed in a test tube, and the polymerization reaction was initiated with a soldering iron. Visual video images were recorded using a camcorder (Handyman video Hi8), and an Amber camera was used to capture InfraRed images. The images were digitized on a Macintosh Power PC 8500.

Temperature measurements were made with unsheathed fine-gauge thermocouples (OMEGA T0.000 COCO-005) and a Strawberry Tree A/D board on a Macintosh IIVx. Temperature profiles were determined by monitoring the temperature at a fixed point. By using the front velocity, the temporal profile was converted to a spatial profile.

Ultrafine silica gel (CAB-O-SIL, Cabot Corp.) was added to a HDDA reaction solution to test the influence of convection on the periodic modes.

IV. RESULTS AND DISCUSSION

A. Effect of passive diluent composition on HDDA fronts

A single-headed spin mode is observed for the HDDA percentage range of 38%–42% (see Table I). Using the IR camera, a bright spot can be detected moving in a helical path along the surface of the test tube. The spot leaves a bright track as it moves; Fig. 3. Using the Bromophenol Blue indicator, the spin can be observed as a pale yellow line moving into the green reactant solution in a spiral fashion.⁴⁷ A helical green spiral was observed in the zone between a spiral and its predecessor, which we propose corresponds to a region of low conversion and thus low radical concentration. This zone gradually becomes pale green as the dye diffuses and reacts with trapped free radicals. (The radical concentration may be as high as 1 mM.⁴⁷) Nevertheless, the polymer rod has the traces of the spin imprinted on the surface.

Upon breaking the polymer rod along its axis, the traces of the spin were found within as alternating translucent and pale sections. This clearly demonstrates that the reaction occurs not only on the surface but also within the bulk of the specimen. The geometry of the reaction zone has to be a

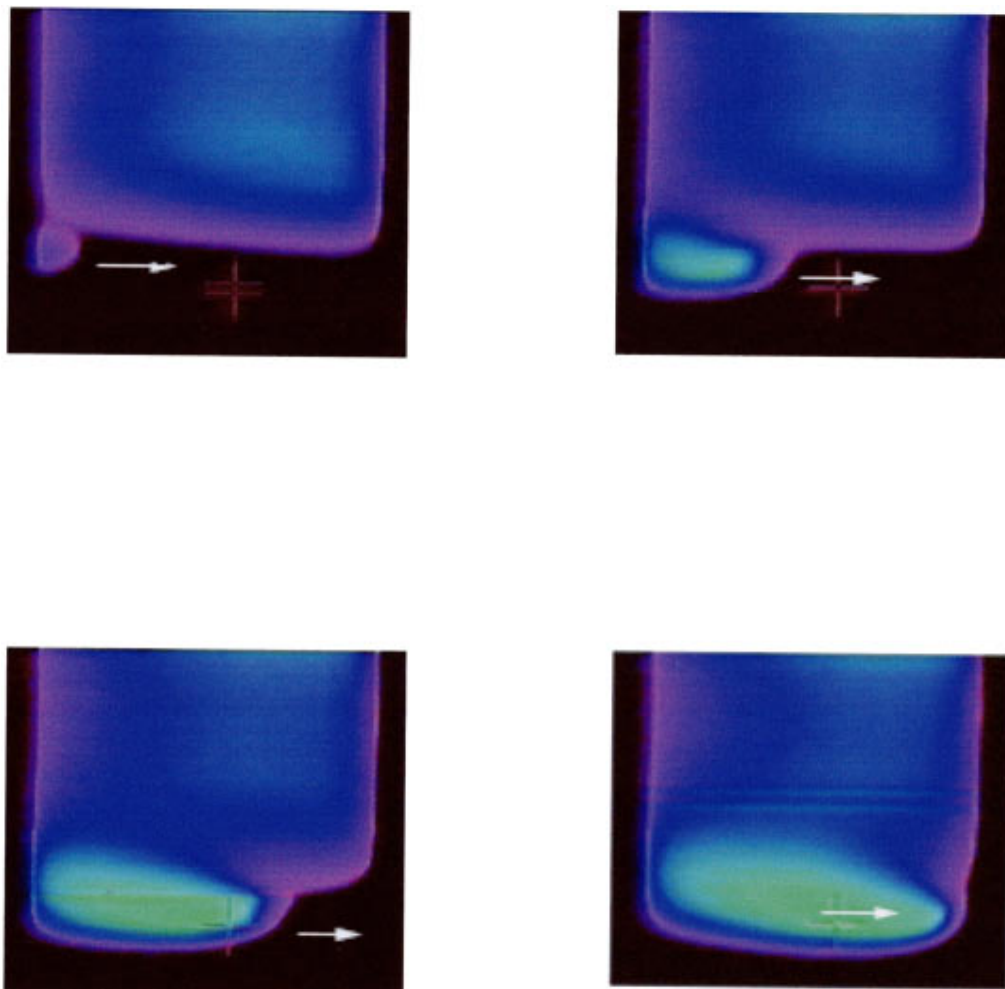


FIG. 3. IR montages of a single-head HDDA spin mode front taken at 20 s intervals. A visual image of a single-head HDDA spin with Bromophenol Blue as an indicator shows dark green and pale yellow spiral traces (Ref. 47).

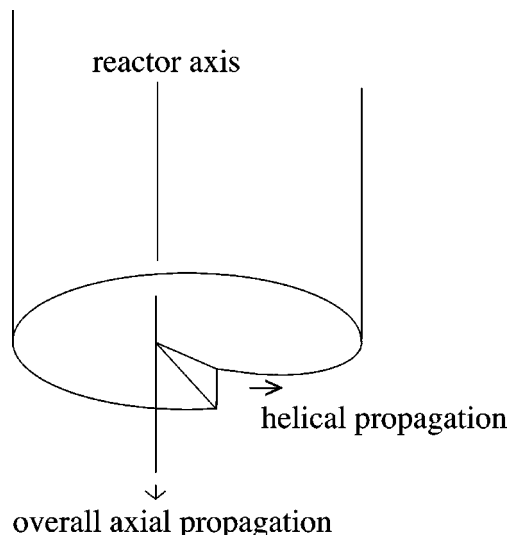


FIG. 4. An illustration of the spin-head motion that would result in the pattern observed inside the polymer rod.

spiraling plane, a pattern obtained only because of the spiral motion of the reaction zone with an axis of rotation passing through the center of the test tube. Figure 4 illustrates the motion that would result in such a pattern. This was confirmed when a reaction was quenched by immersing a tube in ice water.³⁹

The single-head mode polymerization regime becomes double headed when the percentage volume of HDDA is increased into the 42%–46% range. The two spin heads become equidistant to each other as the front propagates, and the sizes of the hot spots are smaller in comparison to the single-head hot spots. What is even more curious is that the two heads are not of the same size. One is smaller than the other; Fig. 5. IR images of these two spin heads show one spot appearing just as its predecessor is disappearing from view. This is different from the images of single head spots, where a spot can be observed as it moves along the surface closer to the camera and takes some time to reappear as it travels along the surface away from the camera view. When the free-radical indicator is used, the two spin heads can easily be visualized. The indicator also shows that the reaction zone occurs in the entire sample, not just the surface. Like the one-headed spin, the two-headed spin mode maintained the spiral direction from the top of the test tube all the way to completion.

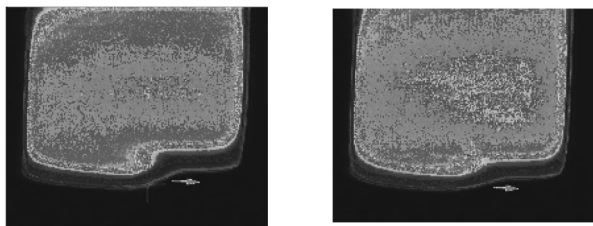


FIG. 5. An IR montage of a double-headed HDDA spin mode. In contrast to the size of a single-headed spin, these heads are smaller. There is also a marked difference in the size of these heads.

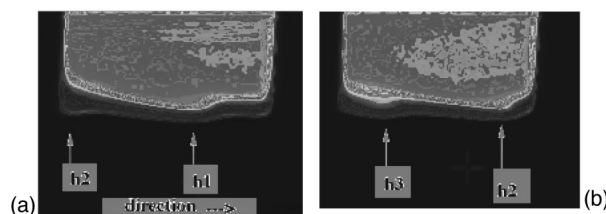


FIG. 6. An IR image of two of the four hot spots of a four-headed spin mode. Only two of these spots, h1 and h2, can be observed at a time because the other two, h3 and h4, are hidden behind (a). After 20 s, h1 disappears and, as h2 is about to disappear, h3 appears, (b).

Four spin heads are observed upon a further increase in the HDDA percentage (46%–49% range). Using an IR camera, only two of these spots can be observed at a time, the other two are not observed as they are hidden behind: Figure 6 shows an IR image of two of the four hot spots. These spots are evenly spaced and maintain the same direction of propagation around the front. The hot spots get even smaller with increasing HDDA percentage, and the spots become increasingly difficult to discern. Eventually the fronts appear flat and seem to pulsate. However, no pure pulsating fronts were observed. It is possible that there is an overlap between spin modes and pulsating fronts, as had been predicted by Sivashinsky⁴⁰ and calculated for frontal polymerization Zeldovich numbers greater than 8.5.⁴⁶ Traces remaining on the surface are annular and almost parallel and could be symptomatic of pulsating fronts. These results are summarized in Table I.

B. Effect of passive diluent composition on TMPTA fronts

When TMPTA was used as the acrylate monomer, with DMSO as the passive diluent, a doubling of spin heads was also observed. However, unlike the HDDA in which an increase in the percentage of the monomer composition eventually resulted in a flat front, multiple spin heads were observed with TMPTA. Beyond four spin heads, subsequent hot spots that did not move in a unidirectional fashion were observed. The heads would collide, Fig. 7, and a reversal in the spin direction was observed. This behavior had been observed in a SHS system studied by Maksimov *et al.*¹¹ However, our observation is the first of its kind observed in a frontal polymerization system. The number of these heads increases with an increase in the percentage composition of TMPTA.

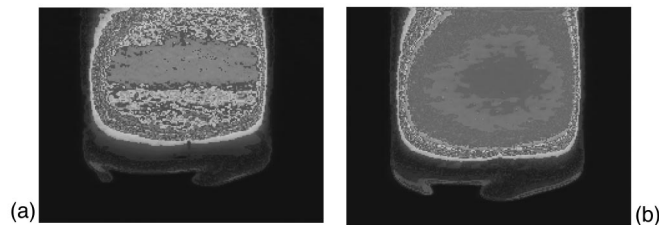


FIG. 7. Images of two TMPTA heads approaching each other in a pulsating symmetric mode (a). These heads get closer to each other after 20 s (b).

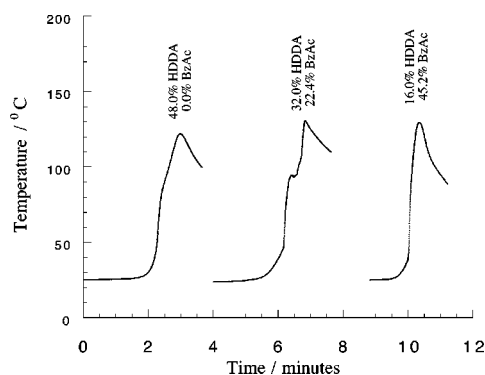


FIG. 8. Temperature profiles showing the dependence of T_{\max} on the percentage composition of the reactant composition. When the total vinyl concentration is kept constant (0.107 M), T_{\max} remains constant, even though the composition of HDDA and benzyl acrylate is varied. The temperatures indicated correspond to the maximum temperatures reached for each HDDA and the benzyl acrylate percentage composition.

A further increase in TMPTA composition resulted in the disappearance of the colliding spin heads. Instead, numerous spots were observed on the entire reactant–polymer interface that appeared rippled when the BPB indicator was used. The IR images showed bright flare-ups ahead of the progressing polymerization front. The observed apparent lack of directional consistency of the hot spots can be characterized as aperiodic. Strunin *et al.* characterized a chaotic propagation mode in SHS,⁵⁰ but we did not perform any rigorous analysis of the time dependence of this behavior.

C. Effect of polymerizable diluent composition

When DEP was replaced by benzyl acrylate as the diluent, T_{\max} was found to be independent of the benzyl acrylate percentage; Fig. 8. Although a change in the front behavior was observed as the percentage of the reactive diluent varied, that change occurred within a broad range of percentage composition as opposed to the rather narrow ranges associated with passive diluents.

The change in front behavior observed with TMPTA and HDDA could be attributed to the changes in T_{\max} and E_{eff} in the Zeldovich equation. By using an inert diluent, these two parameters are altered as a result of changes in the heat release and cross-link density. Inert diluents lower the cross-link density, and thus keep E_{eff} low. The activation energy tends to increase with an increase in monomer conversion.⁴⁸ Dilution also means there is a lower initial concentration of vinyl moieties, and therefore a lower T_{\max} is expected.

Instead of using an inert diluent, a polymerizable diluent, benzyl acrylate, was used. Multifunctional vinyl monomers cross-link extensively at low conversion with a subsequent increase in viscosity. The elevated viscosity restricts the mobility of the terminal ends of polymer chains as well as the motion of unreacted monomers. Dilution with a reactive diluent should lower the degree of cross-linking. By maintaining the initial concentration of vinyl moieties constant, we can alter the degree of cross-linking without changing T_{\max} . Since prior results confirm the dependence of E_{eff} on conversion,⁴⁸ any observed changes in front dynamics, with

TABLE II. Effect of polymerizable diluent composition.

% HDDA	% benzyl acrylate	% DEP	Front behavior
<22	<36.2	>41.8	1 head
22.4–44.8	36.8–44.0	40.8–11.2	2 heads
45.2–48	4.0–0.0	50.8–52.0	4 heads

benzyl acrylate as a diluent, can be ascribed to changes in E_{eff} and/or a change in the energy of activation dependence on conversion.

By maintaining the total vinyl concentration at 0.11 M, single-headed spin behavior was observed below 22% HDDA and 36.8% benzyl acrylate. Two spin heads were observed between 22.4%–44.8% HDDA and 36.8%–44% benzyl acrylate. When the HDDA and benzyl acrylate ranges were shifted to 45.2%–48% and 4%–0.0%, respectively, four-headed spin modes were observed. It is worth noting that Lupersol was kept constant at 4% and DEP percentage varied in accordance with the volume needed to adjust the total volume to 25.0 mL. Table II shows a summary of the above-mentioned results.

D. Periodic modes and convection

Garbey *et al.* predicted that the critical Zeldovich number for the appearance of the first spin mode depended on the viscosity of the unreacted medium.^{51,52} For descending fronts with a solid product, the critical value goes down with increasing convection. The opposite behavior is predicted for ascending fronts.

The addition of CAB-O-SIL to the reaction mixtures substantially increases the initial viscosity. The addition of 5% turns the monomer into a gel. Although a poorly defined spiral trace is observed in the wake of the front, a clearly defined spin head akin to that in Fig. 3 is not observed. It is possible that the pitch of the spin is too small to be observed or that the temperature of the spin head is changed, but, clearly, the qualitative prediction of Garbey *et al.* is confirmed. We note that the opposite behavior was predicted for fronts forming a liquid product and was confirmed by McCaughey *et al.*⁵³ A detailed study of the effect of convection on thermal instabilities is underway.

The disappearance of spin behavior could only be attributed to the increase in viscosity and not changes in the kinetics of the reaction. To verify this hypothesis, two reactions: one with 5.0% Cab-O-Sil and one without, were performed. The resultant front velocities differed by less than 1%. For a system that exhibits reaction-diffusion phenomena, the front velocity can be used to monitor kinetic behavior and any changes in the kinetics tend to be manifest in the front velocity. Differential Scan Calorimetry studies also showed that Cab-O-Sil does not have a significant effect on the rate of polymerization. Thus, it can be concluded that the Cab-O-Sil affects front dynamics by changing only the initial viscosity.

In an earlier study, Pojman *et al.*³⁹ studied spin modes with methacrylic acid, a monoacrylate. Ilyashenko and Pojman found excellent agreement between the experimental phase diagram in the Zeldovich Number- T_0 plane.⁴⁶ How did

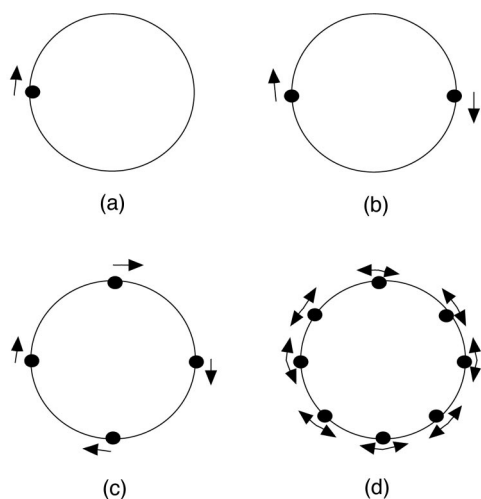


FIG. 9. A schematic summary of the effect of dilution on the behavior of the multifunctional acrylate fronts.

this system agree so well with the standard theory? First, because it is a monoacrylate, the energy of activation of methacrylic acid polymerization is not a function of conversion. Second, the experiments were performed at temperatures below the melting point of methacrylic acid. Thus, the viscosity was infinite, and convection could not play a role.

V. CONCLUSIONS

We have presented results of a period-doubling sequence route to apparently chaotic front propagation. This study shows that the frontal polymerization exhibits complex behavior, the character of which depends on the percentage composition and the nature of both the monomer and diluent. Of all these factors, the variation of percentage composition with respect to an inert diluent was the most convenient parameter for the study of the bifurcation sequence. A schematic summary is given in Fig. 9. A single-head spin is illustrated in Fig. 9(a). However, the behavior becomes more complex as the dilution is decreased. As the percentage of the HDDA increases, there comes a critical percentage at which the number of spin heads doubles, as shown in Fig. 9(b). With a further increase in the HDDA percentage, another doubling of spin heads is observed that results in four spin heads; Fig. 9(c). This trend is typical of a *period-doubling sequence*.

This study shows that the range of the percentage monomer composition, the bifurcation parameter, over which the a particular spin-head mode is sustained, decreases as the number of spin heads increases. Whereas a further increase in HDDA composition eventually leads to flat fronts, TMPTA spin modes become aperiodic, shown in Fig. 9(d). It is interesting that Coffman *et al.*⁵⁴ observed a similar period-doubling behavior in the Belousov–Zhabotinsky reaction, as did Shkuro *et al.*¹⁸ when they studied the propagation of tantalum–carbon combustion fronts. The experiments reported here conform to SHS-based theoretical predictions that front behavior should exhibit a sequence of dynamical

changes upon changing the Zeldovich number. The spin modes observed in this study are very similar to ones observed in SHS systems.

We have made some novel observations. First, changing the degree of cross-linking and thus directly varying the effective energy of activation can control the dynamics. We should note that the Zeldovich number assumes a single energy of activation and thus it is not known how the variation of the energy of activation within the reaction zone affects the system dynamics. Certainly it affects the quantitative agreement between theory and experiment but it may also change the qualitative results as well.

Finally, we have confirmed the prediction of Garbey *et al.*^{51,52} that the viscosity of the unreacted medium can affect the spin mode behavior of a descending front forming a solid product.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the contributions of Gauri Misra and Yuri Chekanov. We are also thankful to Terry Myers (Atochem) for Lupersol. This project was supported by the National Science Foundation (Grant No. CTS-9319175) and by NASA (NAG8-1466).

- ¹U. Anselm-Tamburini and Z. A. Munir, *J. Appl. Phys.* **66**, 5039 (1989).
- ²J. Puszynski, J. Degreve, and V. Hlavacek, *Ind. Eng. Chem. Res.* **26**, 1424 (1987).
- ³A. Varma and J.-P. Lebrat, *Chem. Eng. Sci.* **47**, 2179 (1992).
- ⁴A. G. Strunina, A. V. Dvoryankin, and A. G. Merzhanov, *Combust., Explos. Shock Waves* **19**, 158 (1983).
- ⁵A. V. Dvoryankin, A. G. Strunina, and A. G. Merzhanov, *Combust., Explos. Shock Waves* **18**, 134 (1982).
- ⁶A. G. Merzhanov, A. K. Filonenko, and I. P. Borvinskaya, *Sov. Phys. Dokl.* **208**, 122 (1973).
- ⁷A. Varma, G. Cao, J. P. Lebrat, and M. Morbidelli, *Int. J. Self-Propag. High-Temp. Synth.* **1**, 9 (1992).
- ⁸L. A. Wenning, J.-P. Lebrat, and A. Varma, *J. Mater. Synth. Process.* **2**, 125 (1994).
- ⁹A. G. Merzhanov and I. P. Borovinskaya, *Dokl. Akad. Nauk. SSSR* **204**, 336 (1972).
- ¹⁰A. F. Filonenko, *Int. J. Self-Propag. High-Temp. Synth.* **1**, 19 (1992).
- ¹¹Y. M. Maksimov, A. G. Merzhanov, A. T. Pak, and M. N. Kuchkin, *Combust., Explos. Shock Waves* **17**, 393 (1981).
- ¹²K. G. Shkadinsky, B. I. Khaikin, and A. G. Merzhanov, *Combust., Explos. Shock Waves* **1**, 15 (1971).
- ¹³T. P. Ivleva, A. G. Merzhanov, and K. G. Shkadinskii, *Dokl. Akad. Nauk. SSSR* **239**, 1086 (1980).
- ¹⁴S. B. Margolis, *Metall. Trans. A* **23**, 15 (1992).
- ¹⁵B. N. Novozhilov, *Pure Appl. Chem.* **64**, 955 (1992).
- ¹⁶B. J. Matkowsky and G. I. Sivashinsky, *SIAM (Soc. Ind. Appl. Math.) J. Appl. Math.* **35**, 465 (1978).
- ¹⁷A. Bayliss and B. J. Matkowsky, *SIAM (Soc. Ind. Appl. Math.) J. Appl. Math.* **50**, 437 (1990).
- ¹⁸V. M. Shkuro and G. A. Nersisyan, *Combust., Explos. Shock Waves* **14**, 121 (1978).
- ¹⁹J. A. Pojman, V. M. Ilyashenko, and A. M. Khan, *J. Chem. Soc., Faraday Trans.* **92**, 2825 (1996).
- ²⁰N. M. Chechilo and N. S. Enikolopyan, *Dokl. Phys. Chem.* **230**, 840 (1976).
- ²¹N. M. Chechilo and N. S. Enikolopyan, *Dokl. Phys. Chem.* **214**, 174 (1974).
- ²²N. M. Chechilo and N. S. Enikolopyan, *Dokl. Phys. Chem.* **221**, 392 (1975).
- ²³N. S. Enikolopyan, M. A. Kozhushner, and B. B. Khanukaev, *Dokl. Phys. Chem.* **217**, 676 (1974).
- ²⁴N. F. Surkov, S. P. Davtyan, B. A. Rozenberg, and N. S. Enikolopyan, *Dokl. Phys. Chem.* **228**, 435 (1976).

- ²⁵ K. A. Arutunian, S. P. Davtyan, B. A. Rozenberg, and N. S. Enikolopyan, Dokl. Akad. Nauk SSSR **223**, 657 (1975).
- ²⁶ S. R. White and C. Kim, "Thermochemical modeling of an economical manufacturing technique for composite structures," 1–240, 1992.
- ²⁷ S. P. Davtyan, K. A. Arutyunyan, K. G. Shkadinskii, B. A. Rozenberg, and N. S. Yenikolopyan, Polym. Sci. U.S.S.R. **19**, 3149 (1978).
- ²⁸ Y. Chekanov, D. Arrington, G. Brust, and J. A. Pojman, J. Appl. Polym. Sci. **66**, 1209 (1997).
- ²⁹ Y. Chekanov and J. A. Pojman, Proc. Am. Chem. Soc. Div. Polym. Mat. Sci. Eng. **76**, 290 (1997).
- ³⁰ J. A. Pojman, J. Am. Chem. Soc. **113**, 6284 (1991).
- ³¹ J. A. Pojman, A. Khan, and W. West, Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.) **33**, 1188 (1992).
- ³² J. A. Pojman, R. Craven, A. Khan, and W. West, J. Phys. Chem. **96**, 7466 (1992).
- ³³ J. A. Pojman, I. P. Nagy, and C. Salter, J. Am. Chem. Soc. **115**, 11044 (1993).
- ³⁴ D. I. Fortenberry, A. Khan, V. M. Ilyashenko, and J. A. Pojman, in *Synthesis and Characterization of Advanced Materials*, ACS Symposium Series No. 681, edited by M. A. Serio, D. M. Gruen, and R. Malhotra (American Chemical Society, Washington, DC, 1998), p. 220.
- ³⁵ D. Fortenberry and J. A. Pojman, Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.) **38**, 472 (1997).
- ³⁶ V. A. Volpert, I. N. Mergabova, S. P. Davtyan, and V. P. Begishev, Combust., Explos. Shock Waves **21**, 443 (1986).
- ³⁷ V. P. Begishev, V. A. Volpert, S. P. Davtyan, and A. Y. Malkin, Dokl. Phys. Chem. **279**, 1075 (1985).
- ³⁸ V. Volpert and V. Volpert, Eur. J. Appl. Math. **5**, 201 (1994).
- ³⁹ J. A. Pojman, V. M. Ilyashenko, and A. M. Khan, Physica D **84**, 260 (1995).
- ⁴⁰ G. I. Sivashinsky, SIAM (Soc. Ind. Appl. Math.) J. Appl. Math. **40**, 432 (1981).
- ⁴¹ A. Bayliss and B. J. Matkowsky, J. Comput. Phys. **71**, 147 (1987).
- ⁴² Y. B. Z. A. P. Aldushin, and B. A. Malomed, Dokl. Akad. Nauk SSSR **251**, 1102 (1980).
- ⁴³ B. A. M. A. P. Aldushin, and Ya. B. Zeldovich, Combust. Flame **42**, 1 (1981).
- ⁴⁴ J. B. Zeldowitsch and D. A. Frank-Kamenetzki, Acta Physicochim. URSS **IX**, 341 (1938).
- ⁴⁵ Y. B. Zeldovich, G. I. Barenblatt, V. B. Librovich, and G. M. Makhviladze, *The Mathematical Theory of Combustion and Explosions* (Consultants Bureau, New York, 1985).
- ⁴⁶ V. M. Ilyashenko and J. A. Pojman, Chaos **8**, 285 (1998).
- ⁴⁷ J. Masere and J. A. Pojman, J. Chem. Soc., Faraday Trans. **94**, 919 (1998).
- ⁴⁸ G. R. Tryson and A. R. Shultz, J. Polym. Sci., Polym. Phys. Ed. **17**, 2059 (1979).
- ⁴⁹ K. N. Gray, *Photopolymerization Kinetics of Multifunctional Acrylates* (University of Southern Mississippi, Hattiesburg, 1988).
- ⁵⁰ D. V. Strunin, A. G. Strunina, E. N. Rumanov, and A. G. Merzhanov, Phys. Lett. A **192**, 361 (1994).
- ⁵¹ M. Garbey, A. Taik, and V. Volpert, Q. Appl. Math. **56**, 1 (1998).
- ⁵² M. Garbey, A. Taik, and V. Volpert, Q. Appl. Math. **54**, 225 (1996).
- ⁵³ B. McCaughey, J. A. Pojman, C. Simmons, and V. A. Volpert, Chaos **8**, 520 (1998).
- ⁵⁴ K. G. Coffman, W. D. McCormick, Z. Noszticzus, R. H. Simoyi, and H. L. Swinney, J. Chem. Phys. **86**, 119 (1987).

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