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The effect of reactor geometry on frontal polymerization spin modes

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Using reactors of different sizes and geometries the dynamics of the frontal polymerization of 1,6-hexanediol diacrylate (HDDA) and pentaerythritol tetraacrylate (PETAC), with ammonium persulfate as the initiator were studied. For this system, the frontal polymerization exhibits complex behavior that depends on the ratio of the monomers. For a particular range of monomers concentration, the polymerization front becomes nonplanar, and spin modes appear. By varying the reactor diameter, we experimentally confirmed the expected shift of the system to a greater number of “hot spots” for larger diameters. For square test tubes a “zig-zag” mode was observed for the first time in frontal polymerization. We confirmed the viscosity-dependence of the spin mode instabilities. We also observed novel modes in cylinder-inside-cylinder reactors. Lastly, using a conical reactor with a continuously varying diameter, we observed what may be evidence for bistability depending on the direction of propagation. We discuss these findings in terms of the standard linear stability analysis for propagating fronts. © 2002 American Institute of Physics. [DOI: 10.1063/1.1445436]

In frontal polymerization, a method of producing polymeric materials via a thermal front that propagates through the unreacted monomer/initiator solution, periodic modes can occur at room temperature, depending on the ratio of a difunctional to a tetrafunctional acrylate. We can change the number of “hot spots” or “spin heads” by changing the ratio. We obtained for the first time polymerization fronts in square tubes and found a new mode in which the hot spot propagates as a “zig-zag.” We confirmed the viscosity effects if spin modes occur in descending fronts. We also observed novel modes in cylinder-inside-cylinder reactors. Lastly, using a conical reactor with a continuously varying diameter, we observed what appears to be evidence for bistability depending on the direction of propagation.

I. INTRODUCTION

Frontal polymerization involves the conversion of a monomer into a polymer via a localized reaction zone that propagates as a front, a result of the coupling between thermal diffusion and Arrhenius-dependence of the polymerization kinetics. The process was discovered in Russia in 1972.¹ Frontal polymerization is an organic and more amenable ana-

log of self-propagating high-temperature synthesis (SHS) of inorganic compounds.² SHS has been extensively studied to prepare ceramics and intermetallic compounds. A rich variety of dynamical behavior has been observed, including planar fronts, spin modes,^{3–5} and chaotic reaction waves.⁶ The dynamics have also been studied numerically and analytically.^{7–9} Ivleva and Merzhanov recently performed three-dimensional simulations of spin modes in cylinders.^{10,11}

Due to the lower temperatures involved in the process and to the slower front velocities, frontal polymerization systems are easier to handle than SHS systems for studying the behavior of thermal fronts in condensed media. The work up to 1984 was reviewed by Davtyan *et al.*,¹² and Pojman *et al.* provided an update in 1996.¹³ Along with empirical studies of frontal polymerization systems, different front dynamics were also theoretically investigated.^{13–15} Of particular interest to this study is the spin-mode front propagation 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.

Ilyashenko and Pojman discussed the theory of spin modes as applied to frontal polymerization, and we refer the reader to that work for additional references.¹⁶ We do point out two important features that are related to frontal polymerization. First, the stability of a thermal front with a one-step reaction with energy of activation, E_a , and front temperature T_f is determined by the Zeldovich number, Z ,

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$$Z = \frac{E_a}{RT_f} \left(1 - \frac{I_0}{T_f} \right). \quad (1)$$

The planar mode is stable if $Z < Z_{cr} = 8.4$, and unstable if $Z > Z_{cr}$. By varying the Zeldovich number up to the stability threshold, subsequent bifurcations leading to higher spin mode instabilities can be observed. Secondly, for a cylindrical geometry the number of spin heads or hot spots is also a function of the tube diameter. We point out that polymerization is not a one-step reaction, so that the above form of the Zeldovich number does not directly apply. However, estimates of the effective Zeldovich number can be sometimes obtained even for complex chemistry by fitting the experimental data to formulas derived under the assumption of single-step Arrhenius kinetics.

The first true spin mode for a polymerization system with a constant front velocity was reported by Pojman *et al.*¹⁷ In that work, the frontal methacrylic polymerization exhibited spin modes when the initial temperature was lowered to 0 °C. Spin modes at room temperature were first observed by Masere and Pojman in the frontal polymerization of a diacrylate.¹⁸ The number of hot spots was effected by the front temperature, which was controlled by an inert diluent, and by the degree of crosslinking, which was controlled by varying the ratio of a monoacrylate to a multifunctional acrylate. Masere *et al.* experimentally showed how a change in the front behavior occurred when the percentage of a reactive diluent is varied while keeping T_{max} constant.¹⁹ Manz *et al.* recently used magnetic resonance imaging to reconstruct the path of a single-head spin mode.²⁰

Frontal polymerization has been demonstrated as a method for preparing functionally gradient polymeric materials,^{21,22} temperature-sensitive hydrogels,²³ and may have utility in preparing large composites.²⁴ Reactors in such applications would not be limited to cylindrical geometries and so understanding the different modes that occur in other geometries is interesting because nonplanar modes induce inhomogeneities in the polymer and may not be desirable in the final product.

However, few investigations have focused specifically on the effect of the size and the shape of the reactor on front dynamics in SHS, and we know of no such experimental work with frontal polymerization. Shcherbak performed analysis and numerical simulations for a one-step reaction in a reactor with a square cross section.^{25,26} He reported two modes in addition to the spin mode as seen in cylinders: a “corner mode” in which high temperature regions appeared at two opposing corners and an “annular mode” in which the region of high temperature “is a ring which is first compressed to the center of the specimen, then tends to its surface.” From the side, this mode would manifest itself as “four pairs of foci with elevated temperature moving opposite to each other on the side surface.”

Volpert *et al.* performed a stability analysis of this problem and studied combustion fronts in the $Fe_2O_3 + Zr$ system.²⁷ They observed a mode in which a “hot spot” propagated down the center of each face and then split into two propagating perpendicularly to the overall direction of propagation. Upon reaching the corner the hot spots propa-

gated down the corner and then split, propagating perpendicularly along the face. Upon meeting the hot spot coming from the other direction, the two spots combined and propagated down the face, starting the cycle over. Nonlinear analysis of square cross section samples was performed in the context of combustion synthesis problems by Margolis.^{28,29}

We consider four types of reactors:

- (1) Cylinder;
- (2) Square cross-section tubes (“square reactors”);
- (3) Cylinder-in-cylinder;
- (4) Conical, in which the circular cross section varies linearly along the axis of the reactor. (We note that this has only been possible since the development of gasless initiators^{30,31} because peroxide and nitrile initiators can cause large pressure increases that can rupture large glass reactors or cause unacceptably large voids at ambient pressure.)

Another interesting problem in frontal polymerization, and one that distinguishes it from traditional SHS, is the effect of buoyancy on spin modes. 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.^{32,33} For descending fronts with a solid product, the critical value increases with increasing viscosity. Masere *et al.* confirmed this prediction when they observed that spin modes did not occur at room temperature for descending fronts in which 5% of ultrafine silica gel had been added.¹⁹

In this paper, a comparative study of spin mode behavior in cylinders and in reactors with a square cross section of different sizes was carried out. We observed a new mode, which we call the “zig-zag” mode that occurs in square tubes under the same conditions that produce a four-head spin mode in cylinders. We always observed a simple spiral for the inner cylinder of the cylinder-in-cylinder reactor no matter what mode is observed on the outside annulus. We observed, for the first time, what appears to be bistability in the transition between modes in conical reactors. We discuss these finding in terms of the standard linear stability analysis for propagating fronts. Finally, we confirmed previous reports of the effect of viscosity on spin modes in descending fronts.

II. EXPERIMENTAL PROCEDURE

Dimethyl sulfoxide (DMSO), 1,6-hexanediol diacrylate (90% technical grade; HDDA), pentaerythritol tetraacrylate (PETAC), which contains from 10% to 40% of triester, and ammonium persulfate were purchased from Aldrich and used as received. The ammonium persulfate (initiator) solution, 0.876 M, was freshly prepared before each series of experiments. In order to study the effect of the passive diluent (DMSO) on the HDDA and PETAC fronts, the initiator concentration was kept constant at 8.7×10^{-3} M; only the HDDA-PETAC volumes were increased while the corresponding volumes of DMSO were decreased to keep the final volume of the solution constant at 25 ml.

TABLE I. Effect of passive diluent on HDDA fronts in cylinders and square reactors with PETAC percentage maintained at 20%.

% HDDA	% DMSO	Front behavior in cylinder (16 mm)	Front behavior in square reactor (13 mm)
12	68	1 Head	1 Head
14	66	1 Head	2 Heads
16	64	2 Heads	4 Heads
16.8	63.2	4 Heads	4 Heads
20	60	Flat front	Rippled front

Ultrafine silica gel (CAB-O-SIL, Cabot Corp.) was added to the solution to test the influence of viscosity on the spin modes.

Cylindrical reactors were Kimax 16 mm×125 mm capped test tubes (Fisher) and 20 mm diam test tubes. Square cross section reactors were prepared from Trubore square tubing (Ace Glass, Inc., Vineland, NJ) of either 13 mm (1 mm walls) or 19 mm inner width (2 mm walls). We refer to these as “square reactors.” The square tubes were linked to one end of a Teflon rubber tube through a narrow neck and to a pipette on the other end. The tubing was formed into a U, which allowed the pressure in the reactor to be constant. This apparatus allowed the easy removal of the samples. Each solution was split and part run in the cylinder and the other part in the square tube.

For the cylinder-in-cylinder experiments, the outside tube was a 16 mm×125 mm capped tube, and the inside tube was a 6 mm×124 mm uncapped tube. The conical reactors had a 6 mm diam at one end and a diameter of 25 mm at the other. The length was 125 mm.

A solution of the reactant mixture was placed in the reactor, and the front was initiated with a soldering iron. Infra-Red images of the front were acquired using an Amber IR camera. Visual video images of the samples were recorded using a camcorder (Handyman video Hi8). For the square reactors, two different shots of the test tube were used, side and edge. The edge shot allows one to discern better the movement of the hot spots.

All experiments were performed at ambient temperature (22 ± 1 °C).

III. RESULTS

A. Cylindrical and square reactors

1. Effect of HDDA composition

In order to study how changing the HDDA concentration influences the front behavior, the PETAC percentage was kept constant at 20%, and the initiator concentration was kept constant at 8.7×10^{-3} M. The smaller cylinder and square reactors were used.

As reported in Table I, a single-head spin mode is observed for the HDDA percentage of 12% when the reaction is performed in the cylinder and in the square reactor (Fig. 1). In the cylinder, the IR image shows a bright spot moving in a helical path along the surface of the cylinder and leaving a bright track as it moves. A spiral trace can be clearly ob-

FIG. 1. IR montages of a single-head spin mode front in a cylinder (16 mm) and in a square reactor (13 mm). The white arrows indicate the direction of the motion of the hot spot.

served in the sample; the polymer rod has the traces of the spin imprinted on the surface. For the square reactor, a spot moving in the IR image is also discernable.

Visual inspection of the sample shows a spiral trace inside the square section rod, Fig. 2, which indicates that the front propagates as a spiral. It is also worth noting that the spirals were not close to the surface of the square tubes, unlike the spirals in round test tubes.

When the HDDA concentration was increased, the front behavior in round and square test tubes was the same: Two-headed spin mode and four-headed spin mode are observed. A similar trend was previously observed by Masere *et al.* for the TEMPTA (diluted with DMSO) and HDDA (diluted with diethyl phthalate) fronts with Lupersol 231 as the initiator.¹⁹ Despite the same trend, the concentration range, for different shape tubes, in which these different spin mode instabilities occur is different. For the round test tube, the multiple-headed spin modes are observed for higher monomer concentration.

The two-headed spin mode occurs when the HDDA concentration is increased to 16% in the cylinder, and up to 14% in a square reactor. Figures 3(a) and 3(b) show a schematic view of the modes. As reported in the previous studies, the two heads are not of the same size: one is smaller than the

FIG. 2. A spiral trace inside the square sample from the 13 mm reactor.

FIG. 3. Schematic diagram of the spin head movement in the square reactor: (a) 1 head spin mode, (b) 2 head spin mode, (c) 4 head spin mode ("zig-zag" movement). In all these case, the domain with maximal temperature is a ring inside the square section of the tube.

other.¹⁹ In both reactors, IR images of these two spin heads show one spot appearing just as its predecessor is disappearing from view. Also in this case, the sample shows a spiral trace inside the square section rod like the spiral trace observed in the samples in round test tubes.

A four-headed spin mode was observed in the square reactor for lower HDDA concentration (16%), Table I. However, a significant difference in the behavior of the hot spots was observed for the four-headed spin mode in the square test tube. The side view of the square reactor showed a complex movement of the small heads. When viewed from the face of the square test tube, a "zig-zag" movement of the heads is apparent [Fig. 4]. The hot spot moves from one edge of the test tube and back without going past the edge to the other face. Second, there is a hot spot for each face of the square reactor, and two spots approach the same face and meet at the edge after which the travel away from each other towards the opposite edges.

This description is confirmed when the edge shot image is analyzed. The edge view clearly shows that there is one small head for each edge of the square tube. These heads move from one edge to the other one where they "collide" with the other small head, Fig. 4, and then they reverse the direction of motion, thus describing the "zig-zag" pattern of movement. Moreover, the images captured with the IR camera show that at first the "zig-zag" movement is in phase. Also the visual analysis of the sample shows a different pattern in the spiral trace for sample made in square test tubes when compared to sample made in round test tubes. In the case of square test tube samples, the spiral trace inside the sample is not well defined and not as regular as in the case of the single-head spin mode.

When the HDDA concentration is further increased, a flat front was observed in the cylinder, whereas for the square reactor a rippled front was observed even for high HDDA concentration, Table I. This behavior is similar to the mode observed with TEMPTA fronts in cylinders.¹⁹

FIG. 4. Montages of IR images of the four-headed spin mode in square reactor (13 mm). The edge shot is utilized. The white arrows show the direction of the moving heads. A white line, representing the central corner, is also superimposed to explain the edge view.

2. Effect of PETAC composition

The effect of varying the PETAC concentration on front behavior was studied while the HDDA percentage was kept constant at 12%; the initiator concentration was 8.7×10^{-3} M.

When the PETAC concentration is increased, the same trend described in the preceding section is observed: 1 head spin mode (20%–22% range), 2 heads spin mode (24%), and 4 heads spin mode (26%–28% range), Table II. However, in this case, the different modes are observed in the same concentration range for the cylindrical and square tubes.

Moreover, unlike the previous study in which HDDA concentration is increased until a flat front in the cylinder is observed, a rippled front was observed with PETAC in cylinders. We infer that in this case more small heads closer to each other are present moving in a random fashion. It can therefore be concluded that by increasing the PETAC concentration, the front behavior in square tubes is like the observed behavior when the HDDA concentration is changed.

TABLE II. Effect of passive diluent on PETAC fronts in cylinders and square reactors with HDDA percentage maintained at 12%.

% PETAC	% DMSO	Front behavior in cylinder (16 mm)	Front behavior in square reactor (13 mm)
20	68	1 Head	1 Head
22	66	1 Head	1 Head
24	64	2 Heads	2 Heads
26	62	4 Heads	4 Heads
28	60	4 Heads	4 Heads
30	58	Spin modes	Rippled front
32	56	Rippled front	Rippled front

TABLE III. Effect of reactor size on HDDA fronts with PETAC percentage maintained at 20%.

% HDDA	Cylinder (16 mm diam)	Cylinder (20 mm diam)	Square reactor (13 mm side)	Square reactor (19 mm side)
8	...	1 Head	...	1 Head
12	1 Head	2 Heads	1 Head	2 Heads
16	2 Heads	4 Heads	4 Heads	4 Heads (?)
18	First flat front, then spin modes	...	4 Heads	Rippled front
20	Flat front	Rippled front	Rippled front	Rippled front

One-headed, two-headed, and four-headed spin modes were observed for cylinders and, one-headed, two-headed, and “zig-zag” movement of the spots in square reactors. Table II summarizes the observed behaviors changing the PETAC concentration. When the PETAC concentration is increased above 30%, flat fronts are initially observed immediately after the initiation of the reaction but, after some time, spin modes emerge.

3. Effect of reactor size

Additional experiments were performed in larger reactors. Due to the thickness of the glass, utilizing a larger tube made it more difficult to discern the front behavior with the IR camera. Nevertheless, spin modes were observed in both the bigger round and square test tubes. One-headed and two-headed modes were easy to identify but the four-head spin mode was only discernable with difficulty in the large square reactor.

As shown in Table III and Table IV, for the round test tube, increasing the tube diameter, a shift to higher spin modes was observed. Neglecting heat losses, when the monomer-to-diluent ratio is kept constant, the Zeldovich number is constant too; increasing the diameter of the round tube the system moves to higher spin modes.

It is more difficult to observe the same behavior when experiments are performed in square tubes because the thickness of the glass of the bigger tubes decreases the IR camera's sensitivity. As reported in Table III, it seems that there is a shift to higher spin modes as the dimension of the section of the square tube increases.

The visual images of the samples for the larger square tubes show a spiral trace inside the square, Fig. 5. A comparison of an image with results obtained with smaller square reactors shows the same pattern inside the square rod. So, for the larger square tubes, it can be concluded that the hot hump on the front surface does not propagate completely to the edge.

The “rippled front” is mostly likely a complicated mode, perhaps chaotic but because the temperature variations are so small, they cannot be resolved with the IR camera.

4. Effect of the viscosity

The addition of ultrafine silica gel (CAB-O-SIL) to the reaction mixture substantially increases the initial viscosity of the solution. When the CAB-O-SIL concentration is about 5% (w/v), the reactant mixture becomes a gel.

In this condition no spin modes were observed, and the polymerization front became flat. The visual inspection of the sample also shows an opaque material, and no spiral traces of the spin imprinted on the surface were observed. Recent studies have shown that the disappearance of spin behavior can be attributed only to the increase in viscosity and not in a change in the kinetics of the reaction.¹⁹ The experiments with CAB-O-SIL discussed in this paper confirm the results of the previous studies.

B. Cylinder-in-cylinder reactor

Spin modes were also obtained in a cylinder-in-cylinder reactor. Figure 6 shows a spin mode propagating in the outside tube in the cylinder-in-cylinder experiment. Figure 7 shows the samples obtained when the reaction is completed. We can see a spiral trace imprinted in the polymer rod obtained from the inside tube. The polymer rod of the inside tube was separated from the outside polymer rod by breaking up the glass of outside tube carefully.

The results of the cylinder-in-cylinder experiments show well that a spin head of the propagating front in frontal polymerization is progressing in the internal part of the tube also, which is consistent to the result of Manz *et al.*, where magnetic resonance imaging was used to reconstruct the path of a single-head spin mode²⁰ and consistent with the three-dimensional simulations of Ivleva and Merzhanov.^{10,11}

As shown in Table V, different spin modes between the inside tube and outside tube were obtained. The spin mode of

TABLE IV. Effect of reactor size on PETAC fronts with HDDA percentage maintained at 12%.

% PETAC	Cylinder (16 mm diam)	Cylinder (20 mm diam)	Square reactor (13 mm side)	Square reactor (19 mm side)
20	1 Head	2 Heads	1 Head	1 Head
24	2 Heads	4 Heads (or more)	2 Heads	2 Heads (?)
28	4 Heads	Rippled front	4 Heads	Flat front

FIG. 5. A spiral trace inside the 19 mm square reactor. Notice that the “zig-zag” does not reach to the edges.

the inside tube was a periodic spiral regardless of the spin modes of propagating front in the outside tube. The pitch of the spiral trace in the inside tube was half of that in the outside tube as shown in Fig. 7. We can explain the smaller pitch of the spiral trace in the inside tube by considering that if the spiral head is approximately linear in shape, its pitch is proportional to the radius.

For 16% HDDA we observed an interesting mode in which the heads collide, Fig. 6, and a reversal in spin direction was observed (or the spin heads pass through each other — it is equivalent). This behavior had been observed in a SHS system studied by Maksimov *et al.*³⁴ and was reported by Masere *et al.* for simple cylindrical reactors with TEMPTA/DMSO.¹⁹

We know of no theoretical work on this problem that can help explain the simple spiral in the inner tube but more complicated modes in the outer annulus.

C. Conical reactor

Using a conical reactor with a continuously varying diameter, we observed what may be evidence for bistability depending on how the reactor diameter varied along the di-

FIG. 6. A spin mode of propagating front in the outside tube in the cylinder-in-cylinder experiments. The diameter of outside tube is 16 mm and the diameter of the inside tube is 6 mm. 16% HDDA, 20% PETAC, 9.0×10^{-3} M ammonium persulfate + 0.2 ml of 0.04 M bromophenol blue in DMSO.

FIG. 7. A spiral trace in the polymer rods obtained in the cylinder-in-cylinder experiments. Same composition as in Fig. 6.

rection of propagation. (All fronts were descending.) Two kinds of conical tubes were used: one with the upper diameter 25 mm decreasing to the bottom diameter 8 mm and the other increasing from the upper diameter 6 mm to the bottom diameter of 22 mm. The scheme of the conical reactor experiments is shown in Fig. 8.

The results are summarized in Tables VI and VII. We usually observed the same spin mode in the same diameter region regardless of the direction of propagation, i.e., decreasing diameter or increasing diameter. However, for 16% HDDA, we observed hysteresis in the transition between modes in the two conical shape reactors as compared in Fig. 9. A front propagating from the large to small diameter exhibited a counterpropagating mode in the region of diameter 20 mm but a front propagating from the small to large diameter exhibited a 2 head spin mode at the same diameter. We know of no theoretical work addressing this problem.

IV. DISCUSSION

A. General considerations

We first emphasize that using the Zeldovich number [Eq. (1)] requires the assumption of a one-step, first-order reaction. The trends discussed by Ilyashenko and Pojman (and the works they cite) apply for adiabatic systems.¹⁶ Heat loss can significantly alter the dynamics in frontal polymerization.¹⁷ Nonetheless, we now consider how the observed behavior is at least consistent with our understanding of how the changes would translate into changes in an “effective” Zeldovich number. We do know that the “real” polymerization kinetics stabilizes the fronts compared to what would be predicted from the Zeldovich number calculated from the overall energy of activation and front temperature.³⁵

Masere *et al.* showed that keeping the front temperature constant but varying the ratio of a monoacrylate to a diacrylate the front dynamics changed.¹⁹ They attributed this effect to the dependence of the energy of activation of free-radical polymerization to the degree of crosslinking. Higher concentration of the multifunctional acrylate increased the energy of activation and thus increased the Zeldovich number. The actual problem is more complicated because in a multifunc-

TABLE V. The result of cylinder-in-cylinder experiments on HDDA fronts with PETAC percentage maintained at 20%. Outer tube is 16 mm×125 mm capped cylinder tube and the inner tube is 6 mm×124 mm open tube.

% HDDA	Outer tube		Inner tube	
	Pitch (mm)	Spin mode	Pitch (mm)	Trace mode
12	1.8–2.2	1 Head	0.8–1.2	Periodic spiral
16	1.8–2.2	2 Heads or counterpropagating	0.8–1.2	Periodic spiral
20	1.8–2.0	Rippled front	0.8–1.2	Periodic spiral

tional acrylate polymerization, the energy of activation increases as the degree of conversion increases and so there is not a single energy of activation.

Increasing the total acrylate concentration increases the front temperature, which would increase the Zeldovich number. But increasing the ratio of the HDDA to the PETAC decreases the degree of crosslinking, which would tend to decrease the Zeldovich number. Given that increasing the HDDA increased the number of spin modes, we conclude that the increasing of the front temperature had the greater effect on the Zeldovich number.

B. Theoretical discussion

A complete theoretical description of the polymerization regimes observed in the experiments requires a detailed mathematical study of a relevant model, including both linear and nonlinear stability analyses. Such a study is beyond the scope of this paper. However, some theoretical information about the structure of polymerization waves depending on the geometry of the problem can be obtained from simple general considerations that we present below. These considerations are universal in the sense that they apply not only to polymerization waves but also to other problems.

Let us consider a wave that propagates along the axis of a cylindrical sample, which can be a circular cylinder or a cylinder with a different cross section. Let us introduce a coordinate system that propagates at a constant speed together with the wave, and denote the axial variable by z . If we assume for simplicity that the problem at hand involves no-flux boundary conditions at the lateral surface of the cylinder, then the wave (which we refer to as the basic state) is a function of the single variable z . Suppose that the basic state loses stability, as a control parameter Z [Eq. (1)] exceeds a critical value Z_{cr} , via a pair of complex conjugate

eigenvalues $\pm i\omega$ of the linearized problem crossing into the right half-plane of the complex plane. These eigenvalues correspond to an unstable mode with the wave number that we denote by s_* . Such a stability loss is quite typical of many combustion and polymerization problems (see, e.g., linear stability analyses of polymerization waves in Schult and Volpert³⁶ and Spade and Volpert,³⁷ and the references therein). In this case a Hopf bifurcation occurs, and a new regime of propagation appears instead of the unstable basic state. Sufficiently close to the stability boundary this regime can be represented as

$$T = \hat{T} + \varepsilon T_1 + \varepsilon^2 T_2 + \dots \quad (2)$$

Here T is the quantity of interest, e.g., the temperature in the polymerization wave, which depends on the temporal and spatial variables. The maxima of this function are perceived in experiments as the hot spots. Thus the goal of our simplified theoretical analysis is to determine the location and motion of the maxima. The function $\hat{T}(z)$ in (2) is the basic state. The parameter ε measures the deviation of Z from Z_{cr} (which is typically proportional to the square root of the difference $Z - Z_{cr}$). The function T_1 depends on the time t and all of the spatial variables. The form of this function is determined at the stage of linear stability analysis of the basic state. It is the real part of the product,

$$A e^{i\omega t} \Theta(z) \phi.$$

Here $\Theta(z)$ is the axial dependence of T_1 , which may be different for different problems, and ϕ is the eigenfunction of the Laplacian in the cross section Ω of the cylinder,

$$\begin{aligned} \nabla^2 \phi + s^2 \phi &= 0 \quad \text{in } \Omega, \\ \frac{\partial \phi}{\partial n} &= 0 \quad \text{on } \partial\Omega, \end{aligned} \quad (3)$$

with $s = s_*$. Here ∇^2 is the Laplacian, $\partial/\partial n$ is the normal derivative, and $\partial\Omega$ is the boundary of Ω .

For small values of ε , i.e., close to the stability boundary, T_1 is the dominant correction to the basic state in the bifurcating regime. Since the basic state depends only on the axial variable z , all the information about the maxima of T in the cross section of the cylinder is contained in T_1 . Of course higher order terms in the expansion [Eq. (2)] are also important, in particular, to determine stability of the bifurcating regimes and decide on which regime will occur in case of multiple eigenvalue s_* of the Laplacian.^{38,39} However, it is the T_1 that determines the location of hot spots in the cross

FIG. 8. An image of two conical reactors demonstrating how a descending front in each progressed from large diameter to small diameter in the left reactor and vice versa for the reactor on the right.

TABLE VI. The effect of reactor geometry in the conical tube on HDDA fronts with PETAC percentage maintained at 20%. The upper diameter of the tube is 6 mm and the bottom diameter is 22 mm. Tube length is 125 mm and the front is descending.

% HDDA	Tube diameter (mm) 6–10		Tube diameter (mm) 10–18		Tube diameter (mm) 18–22	
	Pitch (mm)	Mode	Pitch (mm)	Mode	Pitch (mm)	Mode
12	1.3–1.5	Flat	1.5–1.8	1 Head	1.8–2.2	2 Heads
16	1.3–1.5	Flat	1.5–1.6	1 Head	1.8–2.2	2 Heads
20	1.3–1.5	1 Head	1.5–1.8	1 Head	1.8–2.2	Rippled front

section and their movement depending on the geometry of the problem. Below we discuss the structure of T_1 for various geometries that are experimentally studied in the paper.

Let us first consider a circular cylinder of radius b . Then solving the eigenvalue problem (3) and disregarding the dependence of T_1 on z we obtain that T_1 is proportional to

$$e^{i(\omega t \pm n\theta)} J_n(\sigma_{nk}r/b), \quad n=0,1,2,\dots, \quad k=1,2,\dots$$

Here r and θ are the polar coordinates in the circular cross section of the cylinder, J_n is the Bessel function of the first kind of order n , and σ_{nk} is the k th zero of the derivative of J_n . The maxima (and minima) of this function occur at the boundary $r=b$ (in fact, if $k>1$ then there are additional maxima/minima inside, which is due to the structure of the Bessel function). As the first factor shows there are n maxima. They move at a constant speed in the angular direction either clockwise or counterclockwise depending on whether plus or minus sign is taken in the exponent. In order to understand which of the numerous regimes can occur we have to look at the corresponding eigenvalues of the Laplacian. They are $(\sigma_{nk}/b)^2$. The constants σ_{nk} are known. They are (in the increasing order)

$$\sigma_{11} \approx 1.84, \quad \sigma_{21} \approx 3.05, \quad \sigma_{31} \approx 4.20,$$

$$\sigma_{41} \approx 5.32, \quad \sigma_{12} \approx 5.33, \quad \dots$$

The bifurcating regime is the one for which the eigenvalue σ_{nk}/b is equal to s_* . Thus, if b is sufficiently small, then all the eigenvalues are greater than s_* and spinning regimes cannot exist. As b is increased to the first critical value,

$$b_1 = \frac{\sigma_{11}}{s_*},$$

the first bifurcation occurs. Since $n=k=1$ in this case, it is a one-head spinning regime with the hot spot moving on the surface. Further increase in b results in the appearance of 2-head, 3-head, and 4-head spinning regimes with hot spots at the surface at

$$b_2 = \frac{\sigma_{21}}{s_*}, \quad b_3 = \frac{\sigma_{31}}{s_*}, \quad b_4 = \frac{\sigma_{41}}{s_*},$$

respectively. The next bifurcation, however, corresponds to $n=1, k=2$, so that there is only one hot spot on the surface, but there is an additional hot spot inside, which also moves along a helix. The same sequence of bifurcations occurs as the control parameter is increased. In this paper several of the above regimes have been observed.

As nonlinear analysis shows generically there are also solutions that simultaneously involve both clockwise and counterclockwise modes with equal amplitudes.⁴⁰ They are perceived as counter propagating hot spots and have been also observed in our experiments.

Let us now turn to the cylinder-in-cylinder configuration. If the walls of the inner glass tube were conducting heat in exactly the same way as the reactive mixture does, then this geometry would be equivalent to a single cylinder configuration, in which case the same regime would be observed inside and outside the thin tube. The fact that the regimes are different indicates that the glass interferes with the thermal contact between the inner cylinder and the shell. Let us for simplicity consider an idealized case when the glass is a perfect insulator. In this case the processes inside and outside the thin tube can be considered separately. Inside it is a circular cylinder — a geometry already discussed. Outside the thin tube, it is a cylindrical shell that we now consider. As before, we have to study the structure of T_1 . Again, disregarding the dependence of T_1 on z we obtain that T_1 is proportional to

$$e^{i(\omega t \pm n\theta)} [Y'_n(s_{nk}a)J_n(s_{nk}r) - J'_n(s_{nk}a)Y_n(s_{nk}r)],$$

$$n=0,1,2,\dots, \quad k=1,2,\dots$$

Here Y_n is the Bessel function of the second kind of order n , and s_{nk} is the k th zero of the equation,

$$Y'_n(s_{nk}a)J'_n(s_{nk}b) - J'_n(s_{nk}a)Y'_n(s_{nk}b) = 0, \quad (4)$$

TABLE VII. Effect of reactor geometry in the conical tube on HDDA fronts with PETAC percentage maintained at 20%. The upper diameter of the tube is 25 mm and the bottom diameter is 8 mm. Tube length is 125 mm and the front is descending.

% HDDA	Tube diameter (mm) 25–18		Tube diameter (mm) 18–13		Tube diameter (mm) 13–8	
	Pitch (mm)	Mode	Pitch (mm)	Mode	Pitch (mm)	Mode
12	2.0–2.5	2 Head	1.8–2.0	1 Head	1.5–1.8	1 Head
16	2.0–2.5	4 Heads (counterpropagating)	1.8–2.0	2 Heads	1.5–1.8	1 Head
20	2.0–2.5	Rippled front	1.8–2.0	1 Head	1.5–1.8	1 Head

FIG. 9. (a) A front propagating from the large to small diameter with a counterpropagating mode in the region of diameter 20 mm. (b) A front propagating from the small to large diameter with a 2 head spin mode. 16% HDDA, 20% PETAC, 8.9×10^{-3} M ammonium persulfate + 0.15 ml of 0.04 M BPB in DMSO.

which involves Bessel functions of order n . As was the case of the circular cylinder, n determines the number of hot spots rotating along the surface. However, in this case the hot spots may occur at both the inner and outer surfaces. Depending on k there may be additional hot spots inside the cylindrical shell. Now we can try to understand what are the regimes of propagation in the cylindrical shell that can be observed when in the inner cylinder there is a one-head spin. Again, in order to understand which of the numerous regimes can occur we have to look at the corresponding eigenvalues s_{nk} of the Laplacian in the ring [Eq. (3)]. The unstable modes which will grow are the ones for which $s_{nk} < s_*$. Solving (4) in the case $a=6$, $b=16$ (which are the radii used in experiments), we obtain

$$s_{11} \approx 0.09, \quad s_{21} \approx 0.18, \quad s_{31} \approx 0.26, \quad s_{41} \approx 0.33,$$

$$s_{12} \approx 0.34, \dots$$

Since the one-head spinning regime is experimentally observed in the inner cylinder of radius 6, we can conclude that this mode (which corresponds to σ_{11}) is already in the instability region, i.e.,

$$s_* > \frac{\sigma_{11}}{6} \approx 0.3.$$

It is also likely that

$$s_* < \frac{\sigma_{21}}{6} \approx 0.5,$$

since no evidence of a two-head spin was observed in the inner cylinder. Thus, s_* is somewhere between 0.3 and 0.5, so that at least three modes in the cylindrical shell are unstable. They are the modes that correspond to s_{11} , s_{21} , and s_{31} because each of these numbers is less than s_* . Any of them can be realized depending on which mode dominates. This conclusion agrees perfectly well with the experimental observation of one-head and two-head spins in the shell.

The conical geometry is very interesting because the radius of the front continuously changes in the course of propagation, thus allowing us to see dynamic transitions from one regime to another. This is unlike the case of a circular cylinder in which in order to see the behavior for different radii, separate experiments must be performed. However, the conical geometry problem does not belong to the class of problems that can be described by the simple theory, e.g., because even in the case of an adiabatic problem the basic state is not one dimensional. Such a problem could be studied using a perturbation approach under the assumption that the slope of the lateral surface of the cone is sufficiently close to vertical. An example of such a perturbation approach can be found in the work by Matkowsky and Volpert,⁴¹ where outward propagating circular waves in the plane and their stability were studied. However, we do not perform such an analysis here.

Finally, let us discuss the square geometry. Here T_1 is proportional to

$$\sin(\omega t) \cos \frac{n\pi x}{l} \cos \frac{k\pi y}{l}, \quad n, k = 0, 1, 2, \dots,$$

where l is the length of the side of the square, and x and y are the coordinates in the square cross section, $0 < x, y < l$. Let us look at the mode that corresponds to $n=k=1$ and take for simplicity of exposition $l=\pi$. Then the mode that we consider has the form $\sin(\omega t) \cos x \cos y$. For times t such that $\sin(\omega t) > 0$ the function has two maxima located at the edges $x=y=0$ and $x=y=\pi$. For times t such that $\sin(\omega t) < 0$ the function has two maxima located at the edges $x=0, y=\pi$ and $x=\pi, y=0$. Thus with time the location of hot spots periodically changes from one pair of the opposite edges to the other. This leading order analysis does not allow us to observe splitting of the hot spots and their continuous motion to the other pair of edges. It can be seen if higher order terms of the expansion (2) (such as T_2) are taken into account.²⁷ This description corresponds to the experimentally observed zig-zag regime.

V. CONCLUSIONS

In this paper, the effect of the shape and the size of the reactor on spin mode instabilities was investigated, and novel frontal behavior in square test tubes was found. Varying the dilution of the system, i.e., varying the heat release and the crosslink density, which effect the Zeldovich number, a trend like a period doubling in the number of the hot spots was observed. In particular, the four-headed spin mode in square

tubes shows an unusual behavior of the hot spots; a “zig-zag” movement was suggested. It is the first time that this propagation mode has been observed with frontal polymerization.

Moreover, the effect of the dimension of the tube diameter agreed with the expected behavior. The reported experimental results for the round tubes (Tables III and IV) show that the HDDA and PETAC low spin-modes in small tubes become unstable in large tubes and subsequently shift to higher spin modes as the tube diameter is increased. Previous findings about the significant effect of viscosity on spin modes was also confirmed and shown to apply to fronts in square reactors.

We studied frontal polymerization in cylinder-in-cylinder reactors and found a simple spiral in the inner tube no matter what complicated mode was observed in the outer tube. Using conical reactors we observed what appears to be bistability in a spin mode depending on what direction the front propagates. Both of these results are new and illustrate complex and interesting frontal dynamics that can be observed in frontal polymerization.

Using standard results from stability analysis, we show that the observed modes are consistent with what would be expected for each geometry.

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