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Single-head spin modes in frontal polymerization

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The single-head spin mode is the first two-dimensional pattern of self-propagating thermal reaction fronts observed after the planar front loses stability. A "hot spot" is observed to propagate around the periphery of the front. The dynamics of the single-head frontal polymerization regime were studied experimentally, and two novel results were found. The "hot spot" was measured and found to be superadiabatic. The relationship between the rotational velocity and the propagating velocity was found. Experimental data were also compared with the theoretical results based on the linear stability analysis and found to be in a reasonable agreement. © 1998 American Institute of Physics. [S1054-1500(98)01101-X]

Frontal polymerization is a method of producing polymeric materials in which a thermal front propagates through the unreacted monomer/initiator mixture. Spatial and temporal periodic modes of propagation do not occur if a parameter, the Zeldovich number, is below a critical value. High front temperatures, low initial temperatures, or high energies of activation all tend to increase the Zeldovich number and lead to "spin modes" in which a high temperature region (a "hot spot") propagates around the front, leaving a spiral pattern in the product if the front is performed in cylinder. The dynamics of the single-head frontal polarization regime were studied experimentally, and two novel results were found. A "hot spot" was measured and found to have a temperature greater than the adiabatic front temperature. The relationship between the rotational velocity and the propagating velocity showed that the spiral pitch is independent of the tube size, which we confirmed experimentally.

Self-propagating thermal reaction fronts can arise in different exothermic reaction media that possess thermal autocatalysis. Frontal regimes have been realized in gaseous, liquid and solid reaction systems including gasless condensed systems that react to form condensed products. Gasless condensed reactive systems such as frontal polymerization are the subject of this paper. Thermal reaction fronts in condensed media are very interesting and important phenomena for many reasons. Thermal fronts have been used in a process called self-propagating high-temperature synthesis (SHS) to prepare technologically useful ceramics and intermetallic compounds.¹⁻⁶ Furthermore, such fronts demonstrate a rich variety of dynamical behavior.

Many polymerization reactions are highly exothermic and able to support the frontal polymerization regime through the coupling of the exothermicity of the reaction and the Arrhenius dependence of the initiator decomposition.^{7,8}

Thus frontal polymerization is a mode of converting monomer into polymer via the spreading of localized reaction zone that propagates as a front.

Stationary planar front propagation was the first frontal polymerization regime studied in detail.^{7,9-12} The stationary regime, however, is not the only possible mode of frontal polymerization. Similar to some combustion processes,¹³⁻¹⁵ different patterns arise in the polymerization fronts. Despite a rich variety of frontal polymerization modes,^{7,12} one of them deserves special attention. It is the single-head spin mode, the first two-dimensional pattern of self-propagating thermal reaction fronts observed after the planar front loses stability. This mode reflects all the fundamental features of frontal dynamic behavior, and it is most convenient to be studied experimentally.

We have observed the single-head spin mode during frontal polymerization of methacrylic acid and frontal curing of epoxy resins.⁷ For two other polymerization systems, the appearance of this regime has also been reported.¹⁶⁻¹⁸ It should be mentioned that such behavior had been first observed in numerous cases of gasless combustion.^{13,19} In this work we report an explanation of some fundamental features of spin modes; namely, the superadiabatic temperature profile, the relationship between the rotational and propagation velocity and a stability diagram.

The one-head spin mode manifests itself as a small hot hump on the front surface adjacent to the tube wall of the cylindrical sample. During front propagation, the hump moves along the perimeter of the sample in a spiral fashion. The infrared and visual images of a spin mode of methacrylic acid polymerization are shown in Fig. 1 and Fig. 2. It can be seen from the infrared image that the spin head has a higher temperature than that of the surrounding medium. At an initial monomer temperature of 0 °C, the spin head moves downward with a velocity of 0.66 cm/min and completes one revolution in 50 s. Spin modes were observed experimentally during frontal polymerization of methacrylic acid containing 2 w/w, % benzoyl peroxide as a thermal free-radical initiator.

FIG. 1. A montage of infrared images of a single-head spin mode in a 2.2 cm diameter tube. Frame numbers correspond to time in seconds.

In this reactive medium, spin modes appear when its initial temperature is lowered down to 0 °C (Fig. 3). At these conditions flat stationary fronts become unstable, and spin modes develop. These modes have nonuniform radial temperature distributions that are demonstrated by their temperature profiles (Fig. 3). (Detailed descriptions of the experimental technique have been presented elsewhere.^{7,12})

The simplest model reflecting basic transport and dynamical behavior of adiabatic thermal fronts in the cylindrical geometry can be written as a heat conductivity equation with a reaction heat source along with the equation of first-order reaction kinetics

$$\frac{\partial \mathbf{T}}{\partial t} = \kappa \left(\frac{1}{\mathbf{r}} \frac{\partial}{\partial \mathbf{r}} \mathbf{r} \frac{\partial \mathbf{T}}{\partial \mathbf{r}} + \frac{1}{\mathbf{r}^2} \frac{\partial^2 \mathbf{T}}{\partial \varphi^2} + \frac{\partial^2 \mathbf{T}}{\partial z^2} \right) + \frac{\Delta \mathbf{H}}{\rho c_p} \frac{\partial \mathbf{C}}{\partial t}, \quad (1)$$

FIG. 2. A visual image of the poly(methacrylic acid) sample formed during the single-head spin regime. The scale is in centimeters.

FIG. 3. The temperature profiles determined for the methacrylic acid fronts at an initial temperature of 25 °C (profile 1) and 0 °C (profiles 2 and 3).

$$\frac{\partial \mathbf{C}}{\partial t} = -\mathbf{k}_0 \mathbf{C} \exp(-\mathbf{E}/\mathbf{RT}). \quad (2)$$

Boundary conditions:

For $0 \leq z \leq \infty$, $0 < \mathbf{r} < \mathbf{a}$, $0 \leq \varphi \leq 2\pi$:

$$z=0: \quad \mathbf{T}=\mathbf{T}_m, \quad \mathbf{C}=0,$$

$$z=\infty: \quad \frac{\partial \mathbf{T}}{\partial z}=0, \quad \mathbf{C}=\mathbf{C}_0,$$

$$\mathbf{r}=\mathbf{a}: \quad \frac{\partial \mathbf{T}}{\partial \mathbf{r}}=0.$$

Initial conditions: $z=0$: $\mathbf{T}=\mathbf{T}_m$; $0 < z < \infty$: $\mathbf{T}=\mathbf{T}_0$.

Here κ is thermal diffusivity, c , ρ , $\Delta \mathbf{H}_p$ are the heat capacity, density and reaction enthalpy, and $\mathbf{k}_0$, $\mathbf{E}$, $\mathbf{C}$, $\mathbf{T}$ are the frequency factor, activation energy, concentration and temperature, respectively.

Although this model is simple and convenient for numerical simulations, it is not acceptable for the analytical study of thermal fronts and their stability. Equations (1) and (2) do not have a stationary propagating front solution be-

FIG. 4. The neutral stability curve for the fronts of a first-order chemical reaction.

FIG. 5. Universal map of the thermal front stability. The parameter Du/κ is the dimensionless diameter of the sample, where D is the physical diameter, u the front velocity and κ the thermal diffusivity. The dashed line (1) relates to the experimental data and shows the methacrylic acid front's transition from planar stability to the single-head spin mode as the initial reactant's temperature is decreased.

cause of the reaction term, i.e., homogeneous reaction occurs throughout the bulk. Thus, additional simplifications are necessary to solve them analytically; namely, the infinitely narrow reaction zone approximation is used that was developed for gaseous combustion^{20,21} and applied later for gasless combustion in condensed media. Using this approximation, analytical equations for front velocity were derived,²² linear stability analysis for one,^{23,24} two²⁵ and three^{26,27} dimensional cases performed, and a mathematical model providing the transition from a distributed Arrhenius source term to a δ -function reaction term was developed.^{24,26} A subsequent mathematical development of the problem dealt with more complex and precise models^{28–30} and the application of bifurcation theory to the study of the nonstationary modes.^{24,30–34}

The statement of the problem in terms of the linear stability of the flat stationary propagation front starts from the analysis of thermo-diffusional stability of laminar flames.³⁵ To examine some of our experimental data we consider and develop results of linear stability analysis toward experimentalists' interests. The first important result of linear stability analysis relates to the dispersion equation and the curve of neutral stability shown in Fig. 4

$$K = \sqrt{Z^2 - 6Z - 8 \pm \sqrt{Z^4 - 12Z^3 + 36Z^2 - 32Z}}. \quad (3)$$

Here, K is the wave number, and Z is the Zeldovich number, defined in Eq. (4)³⁵

$$Z = E(T_m - T_0)/RT_m^2. \quad (4)$$

We invoke the necessary conditions for the appearance of new solutions in the case of the cylindrical geometry of the test tube²⁶ to build a universal mode map (Fig. 5) and a mode map in the tube diameter-Zeldovich number plane using kinetic data for methacrylic acid fronts (Fig. 6). The dashed line in Fig. 5 relates to the experimental data and

FIG. 6. Calculated stability diagram for methacrylic acid fronts as a function of the Zeldovich number and the tube diameter. $E = 18 \text{ kcal mol}^{-1}$, $\kappa = 0.001 \text{ cm}^2 \text{ s}^{-1}$; $T_m - T_0 = 200^\circ \text{C}$.

shows the methacrylic acid front's transition from planar stability to the single-head spin mode domain as the initial reactant's temperature is decreased. Note also that this map shows the existence of the "pure" single-head spin mode domain without an accompanying one-dimensional pulsation mode, exactly as observed experimentally. The map in Fig. 6 shows the expected mode appearance as a function of tube diameter.

We were not able to match this dependence quantitatively with experiments with the single-head spin mode in both 16 and 25 mm tube diameters (Fig. 7). Both spirals had the same pitch though. It is worth noting, however, that the number of spin heads observed in the experiments increased along with the increase of the test tube diameter starting from 25 mm. There is one more single-head mode characteristic that can be extracted from the linear stability analysis and compared with the experimental data. It is the pitch of the single-head spiral trajectory. Using the angular velocity of the spin head from linear stability analysis²⁶ and combining it with linear front velocity,²² we obtain the equation for the spiral pitch

$$L = \sqrt{\frac{\kappa}{k_0 \exp(-E/RT_m)}} \times \frac{16\pi}{\sqrt{Z^2 - 6Z + \sqrt{Z^4 - 12Z^3 + 36Z^2 - 32Z}}}. \quad (5)$$

Using the same reaction parameters (Fig. 6) and assuming that the frontal polymerization system crosses the stability boundary at $Z = 8$ we found the pitch to be equal to 0.5 cm. The corresponding experimental pitch can be estimated from Fig. 2, and it is in reasonable agreement with calculations.

We also note the close similarity of the patterns with experimentally observed single-head spin modes in SHS¹³ and in our experiments and the perturbed solution for the temperature. The temperature perturbation consists of two

FIG. 7. A comparison of poly(methacrylic acid) samples formed during the single-head spin modes in 25 and 16 mm diameter tubes. The spirals have very similar pitches.

three-dimensional temperature extrema adjacent to the test tube walls with super- and subadiabatic temperatures. Such a temperature configuration spins around the z axis with constant angular velocity.²⁶

The existence of the single-head spin mode requires a physical explanation, especially because of a common opinion about the stabilizing role of thermal conductivity in the preheating zone. The qualitative concept and discussion of thermo-diffusional stability of combustion waves takes its origin from the works of Zeldovich.³⁵ According to that concept, we should consider an arbitrarily curved front, as shown in Fig. 8. Indeed, the convex part of the front set against the cold reactant's zone is in thermally unfavorable conditions to survive and grow, and it should be slowed down and dampened by conductive heat transport. For the similar reason, a concave part of front will rush to grow in. Thus, acting alone, thermal conductivity leads to dampening of random front perturbations.^{14,35}

In fact, a spin head has the highest temperature on the front surface (Fig. 3). Moreover, when a front is found to be below the critical conditions, any geometrical perturbation of the front surface will be accompanied by a temperature redistribution in the front as follows from the analysis above. In other words, being a convexity of the front surface toward "cold" reactants the spin head has the temperature that exceeds the adiabatic reaction temperature. That leads to a greater chemical reaction rate in the spin head than anywhere else in the front. This physically explains the ability of the spin head to survive under the unfavorable heat transport circumstances described above.

The appearance of a superadiabatic temperature spin head does not violate conservation of energy. At first, non-uniformly preheated monomer in the spatially nonuniform and nonstationary temperature field of heat conductivity zone can react explosively, overshooting the adiabatic temperature. Second, side by side with a superadiabatic spin head, there is a location (spot) in the front with a temperature below the adiabatic value—something similar to a "cool spin hollow." Actually, the sample in the Fig. 2 consists of two

FIG. 8. A schematic representation of a perturbation to a planar front. Note the convex and concave regions.

spirals. The first one is opaque and formed at lower temperature, and the second one is transparent and formed at higher temperature, which also happens to be closer to poly(methacrylic acid)'s glass transition temperature, thus providing for more transparency.

The qualitative analysis of temperature profile dynamics even for the one-dimensional case, which is merely a projection of a spin mode, is helpful to understand how fronts under critical conditions lose their stability. The temperature profile of the stationary propagating reaction front reflects the heat balance between the heat production caused by the chemical reaction and the heat conductivity sink in each point of the reactive medium. Such a balance can be cited theoretically for systems under critical conditions too. However, any positive temperature perturbation in the reaction zone irreversibly destroys that balance because it leads to the additional reaction heat release exceeding the intensity of the growing heat conductivity flux. In other words, the temperature fluctuation increases both terms of the heat balance mentioned above. Beyond the critical conditions, however, the Arrhenius reaction heat term in the reaction zone becomes quite sensitive and grows more rapidly as the temperature increases than do losses from heat conductivity. Finally, the reaction zone undergoes a thermal runaway with a subsequent relaxation period. Then, again, the temperature profile sharpens and explodes, reaching the imaginary stationary temperature profile. Gradually the system develops new non-stationary regimes. It is interesting that the thermal propagating fronts themselves can be considered as localized thermal runaways restricted by cold reactants on one side and by hot product from another. Thus, figuratively speaking, the spin mode is a "second order thermal runaway."

Returning to the experimental temperature profiles in Fig. 3, we would like to comment on the difference between the second and third profiles, which relates to the single-head spin regime. The unusual inflection in profile 3 shows that the thermocouple in this case was missed by the spin head and instead encountered the cold region spinning behind the hot spin head.

Numerous computer simulations of one-, two-, and three-dimensional cases provide clear conceptions of temperature dynamics of propagating thermal fronts.^{5,27,36–38}

All features of thermal unstable front behavior such as superadiabatic temperatures, cold spots with temperatures lower than the adiabatic temperature, and thermal explosions in the reaction zones, were found during those numerical studies of nonstationary front modes. Thus, there is reasonable agreement between linear stability analysis, numerical simulations and experimental data regarding a single-head spin mode. That makes the single-head spin mode, as well as other periodic modes, more understandable and justifies the linear stability analysis as a powerful tool to study nonstationary modes of frontal polymerization.

In summary, we have analyzed the single-head spin mode that occurs in frontal polymerization and explained the unusual temperature profile it exhibits. The relationship between the angular velocity of the hot spot and the front velocity was calculated and found to agree well with experiments. The experimental data were also compared with the results of linear stability analysis and found to be in reasonable agreement.

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