Dynamics of Thermal Frontal Polymerization

John A. Pojman

Department of Chemistry & Biochemistry

Ad Maiorem Poimanorum Gloriam

Where in the World is USM?

Hurricane Katrina: A Disaster?

Top Ten Advantages of Losing your House and all your belongings to Hurricane Katrina

- 10. You don’t have to pay for electricity.
- 9. You don’t have to pay for phone.
- 8. You don’t have to cut the grass.
- 7. You don’t have to cook something for the neighborhood “Night Out Against Crime”
- 6. You don’t have to clean the house again.
- **5.** You don’t have to decide how to remodel the patio.
- 4. You don’t have to decide what type of curtains to put in the living room.
- 3. You don’t have to worry about gaining weight and not fitting into your 25 suits.
- 2. You will get a brand new house and new clothes courtesy of the Federal Government!
- **1. You don’t have to cook Christmas dinner for the relatives.**

NONLIN listserver

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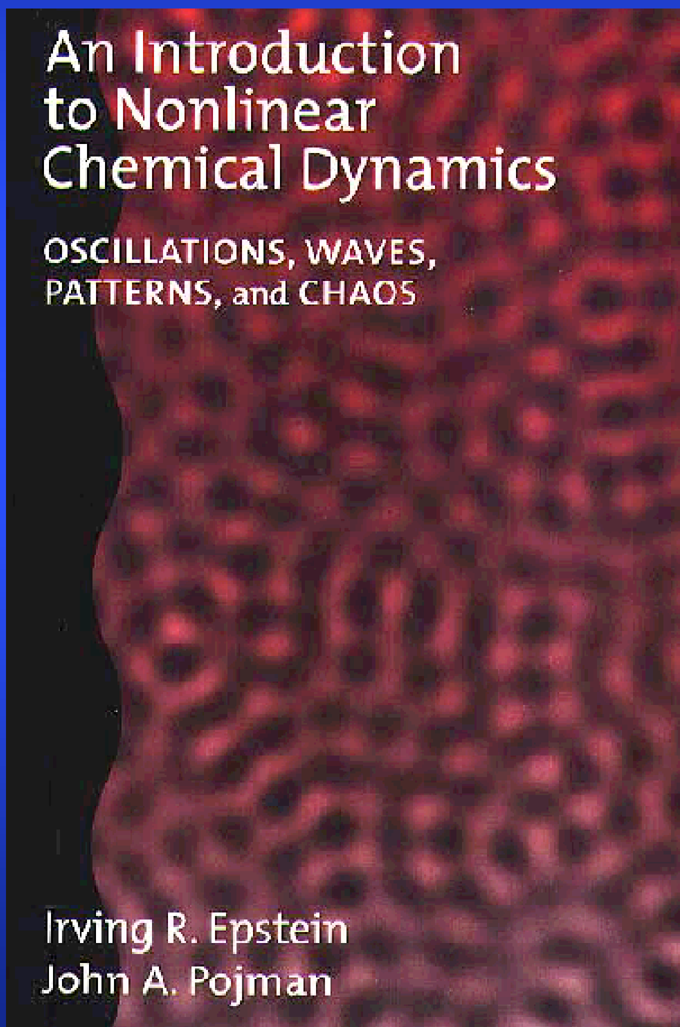
for information, send email to

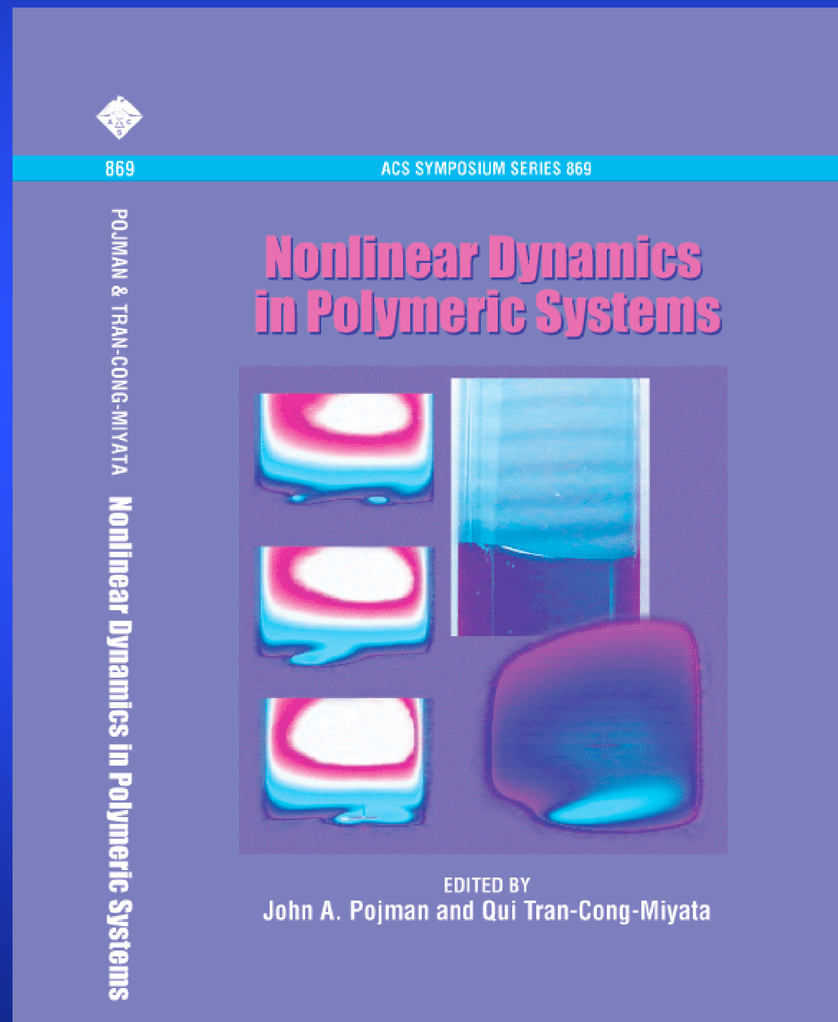
john@pojman.com

or give me your business card

For More Information....

www.pojman.com





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John A. Pojman

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www.pocketprotectors.info

The Pojman Pocket Protector Collection

551 and still growing!

If you want to contribute to the collection, contact J. Pojman about making a donation.

To visit Pojman www site.

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Ever-Clean Pocket Protector

Pocketector

Sta - Kleen

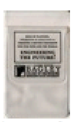
Nerd Pride

University of Akron

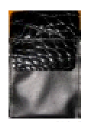
USM Chemistry

Pojman Research Group

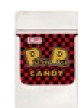
Noetic Technologies



Bagley College of Engineering



Alligator Skin PP



Push Pop candy

NASA

What is Frontal Polymerization?

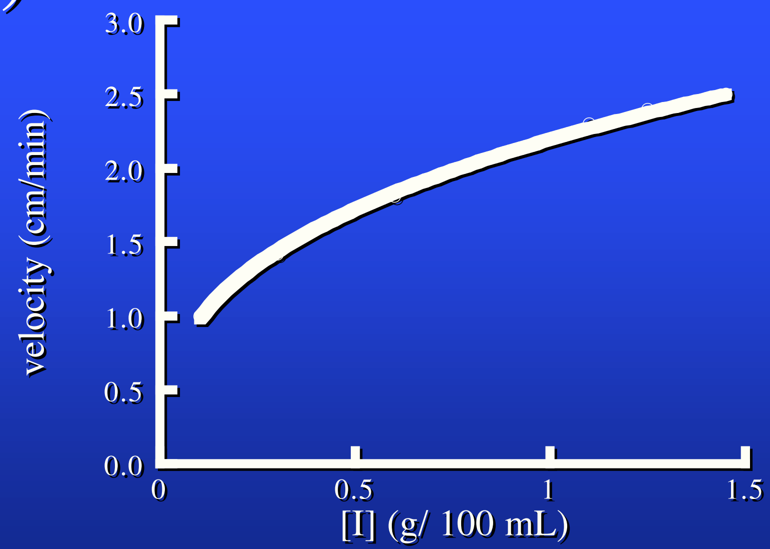
- **Isothermal frontal polymerization** (IFP) is the slow growth of a swelled polymer solid in contact with its monomer, aka, **interfacial gel polymerization**

- **Thermal frontal polymerization** is the coupling of the heat release of polymerization with the Arrhenius dependence of the reaction rate in an unstirred system, i.e., "liquid flame".

- Frontal Photopolymerization, a localized reaction driven by the flux of light.

Thermal Frontal Polymerization

- discovered in 1972 by Chechilo and Enikolopyan at Institute of Chemical Physics (Chernogolovka, Russia)
- used methyl methacrylate under high pressure (> 3500 atm)



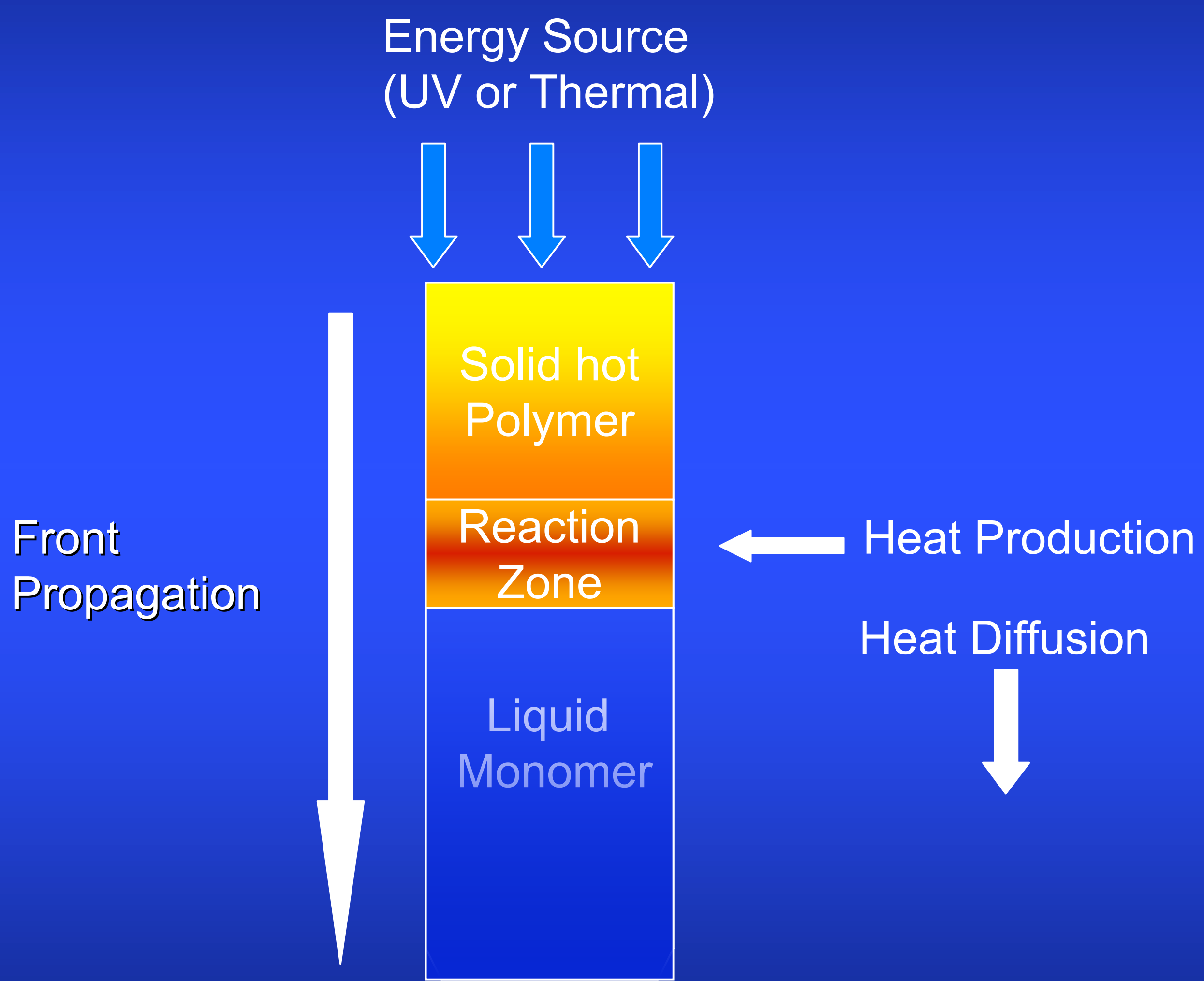
Thermal FP: Analogous to Self-Propagating High Temperature Synthesis (SHS)

- discovered by Merzhanov in 1967

Nickel-Aluminum gasless combustion

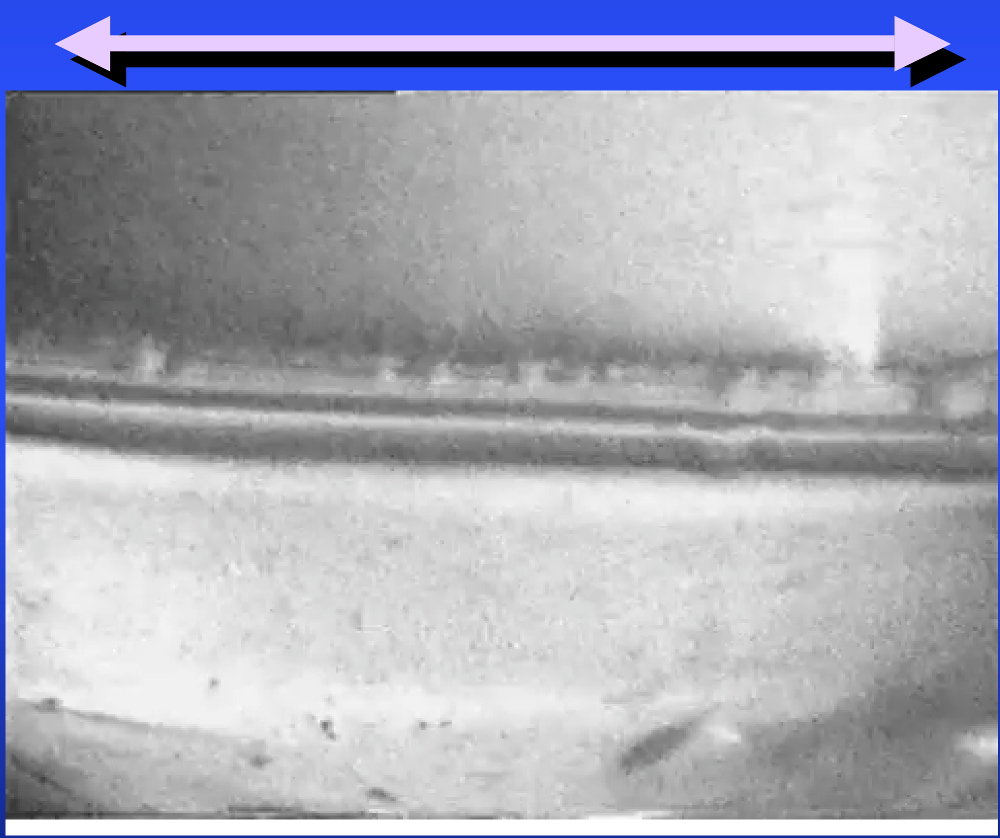
courtesy of Arvind Varma (Notre Dame)

Frontal Polymerization Scheme

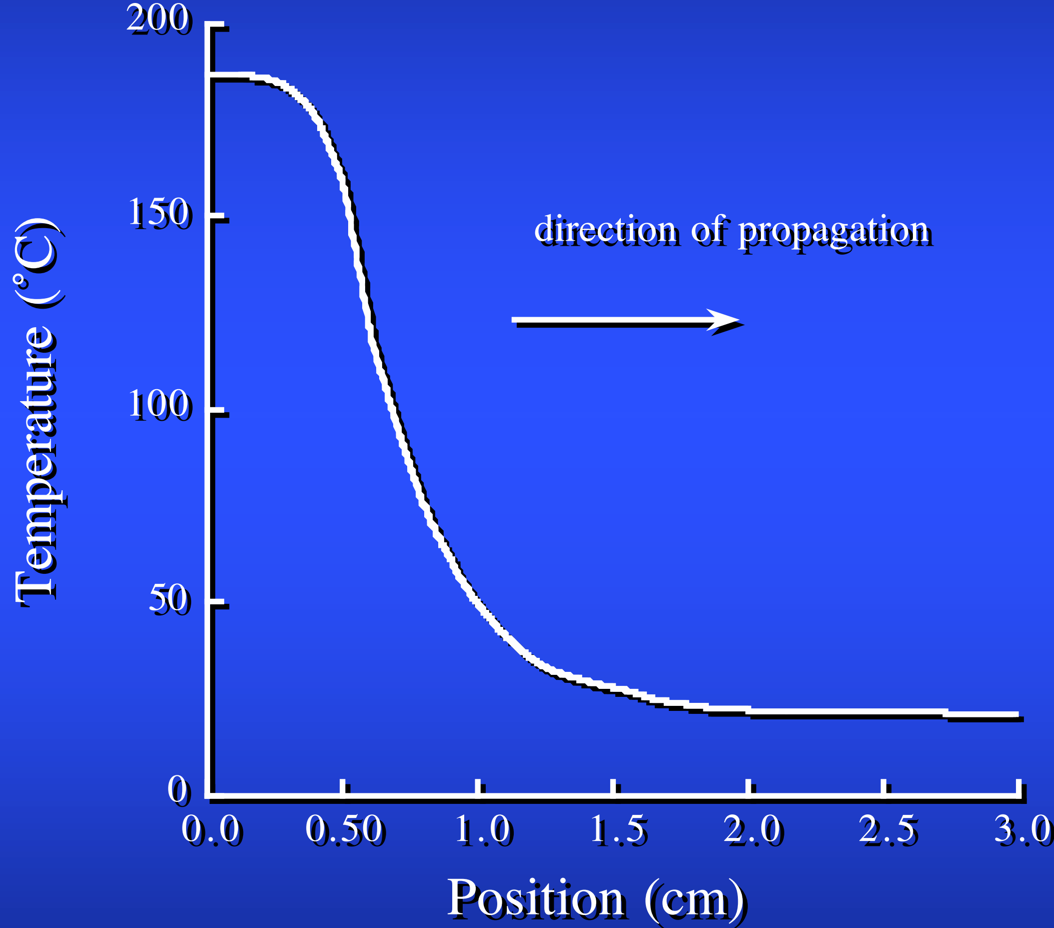


Basic Phenomenon: liquid/solid

methacrylic acid with 5% initiatior

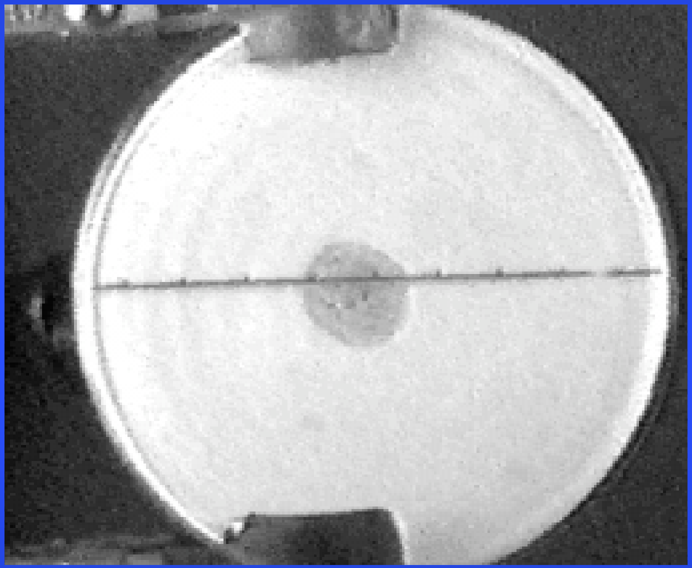


Sharp Temperature Gradients



benzyl acrylate front with CAB-O-SIL

Works with Solid Acrylamide



acrylamide/persulfate in Petri dish

Will propagate at 77 K!

What’s it good for?

- Preparation of functionally-gradient materials
- “Cure on demand” -- a “superfast Bondo”
- Construction applications
- Unlimited depth of cure
- Studying nonlinear phenomena

Chemical Anchors

U.S. Patent Mar. 18, 2003 US 6,533,503 B2

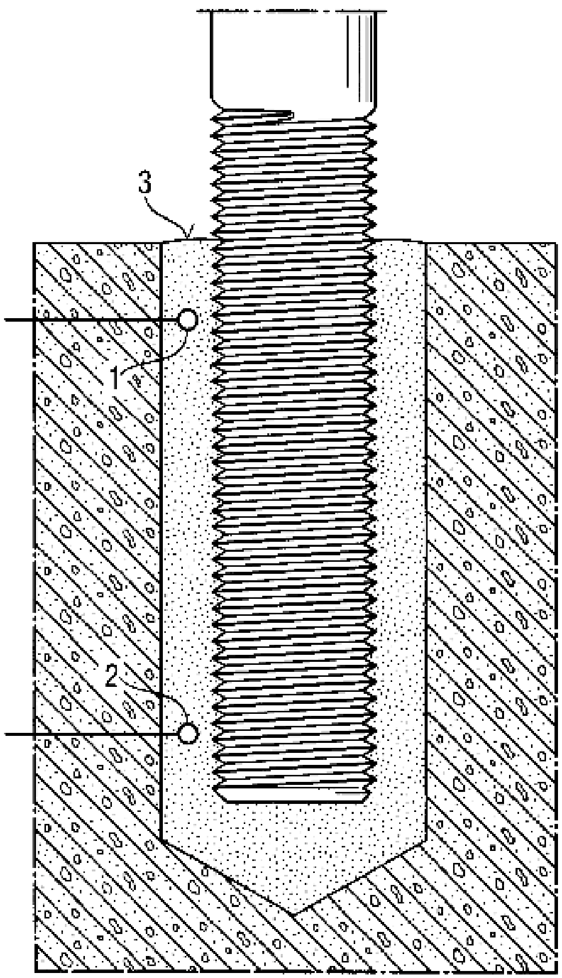


Fig. 1

MORTAR COMPOSITION, CURABLE BY FRONTAL POLYMERIZATION, AND A METHOD FOR FASTENING TIE BARS

FIELD OF INVENTION

The object of the present invention is a mortar composition, which can be cured after thermal initiation by frontal polymerization, as well as a method for fastening tie bars, reinforcing steel or the like in solid substrates using this mortar composition.

There is therefore a need for a mortar composition, which has a very long pot life and the curing of which can be initiated selectively at a desired time. By these means, it became possible initially to provide a large number of boreholes with the mortar composition, subsequently to introduce and adjust the fastening elements and then to initiate the curing, as a result of which it becomes possible to attain an optimum and largely identical curing and, with that, largely identical pull-out strengths of the fastening elements that have been mounted.

HILTI GMBH

43% Clay Filler

TMPTA and Luperox 231

Frontal curing in porous stone

TMPTA + AIBN in pumice

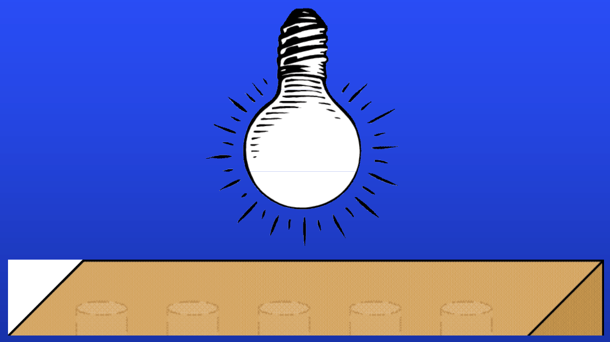
Vicini, S.; **Mariani**, A.; Princi, E.; Bidali, S.; Pincin, S.; Fiori, S.; Pedemonte, E.; Brunetti, A. "Frontal Polymerization of Acrylic Monomers for the Consolidation of Stone," *Polymers for Advanced Technologies* **2005**, *16*, 293-298.

So easy, a five-year old can do it.

- 

Development of a UV-initiated FP-Curable Wood Putty

- Current wood putties require many hours to cure
- Method to fill hole 1 cm diameter to a depth of 1.5 cm in 7 seconds.
- A putty was prepared that could be cured in 12 seconds.
- Cured composite could be sanded and stained.



Patent pending

Final Result

- A putty was prepared that could be cured in 12 seconds.
- Cured composite could be sanded and stained.

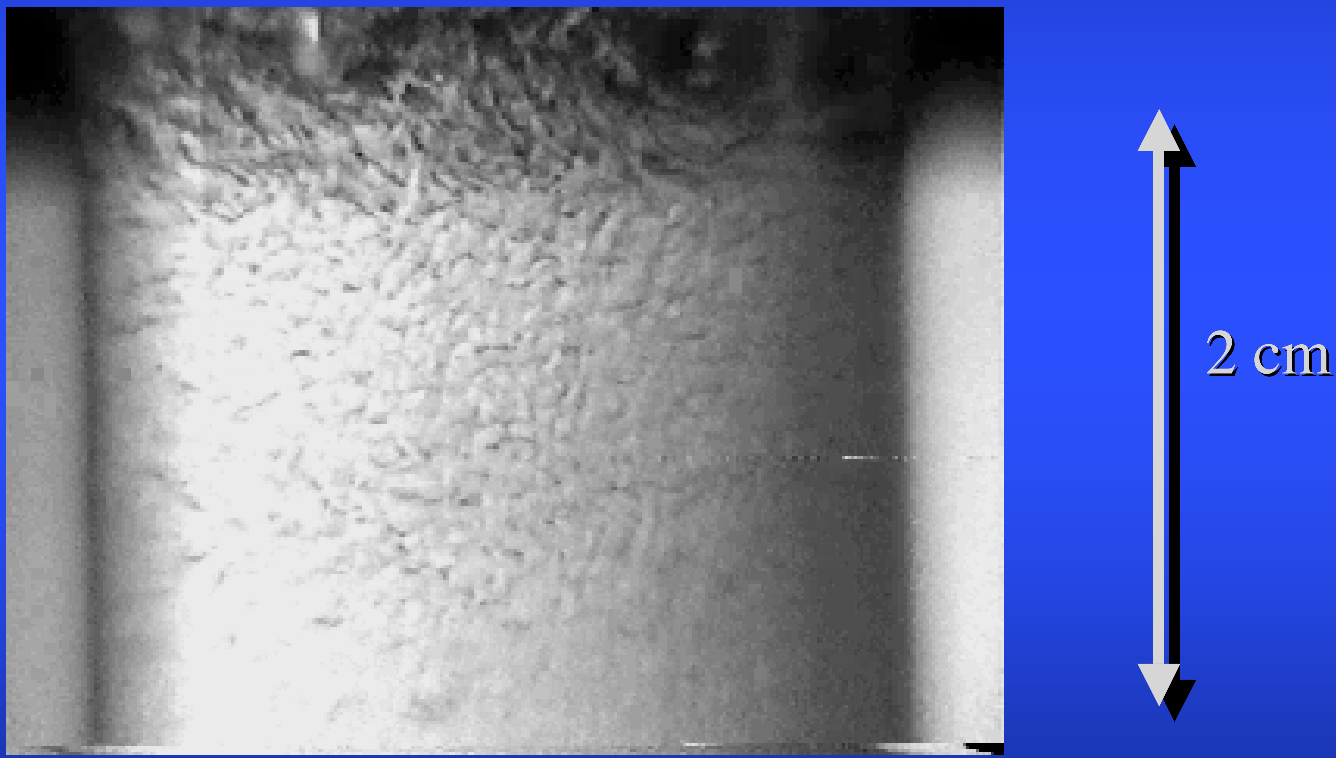
Interferences for Frontal Polymerization

- convection
- periodic modes of propagation
  - “spin modes”

Two Cases for Convection

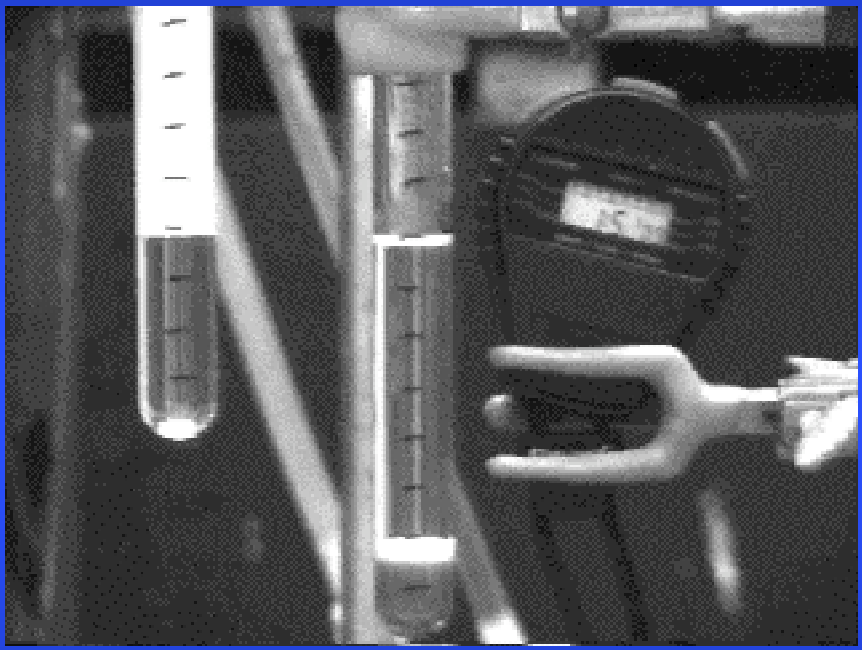
- liquid monomer converted to hot liquid polymer ("liquid/liquid" or thermoplastic)
- liquid monomer converted to hot solid polymer ("liquid/solid" or thermoset)

Liquid-Liquid:
Rayleigh-Taylor Instability

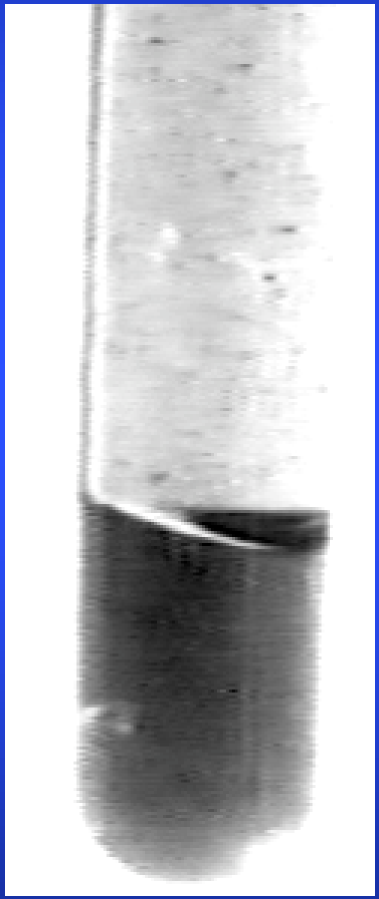


Can destroy front with molten polymer

Simple Convection in Liquid/Solid Front

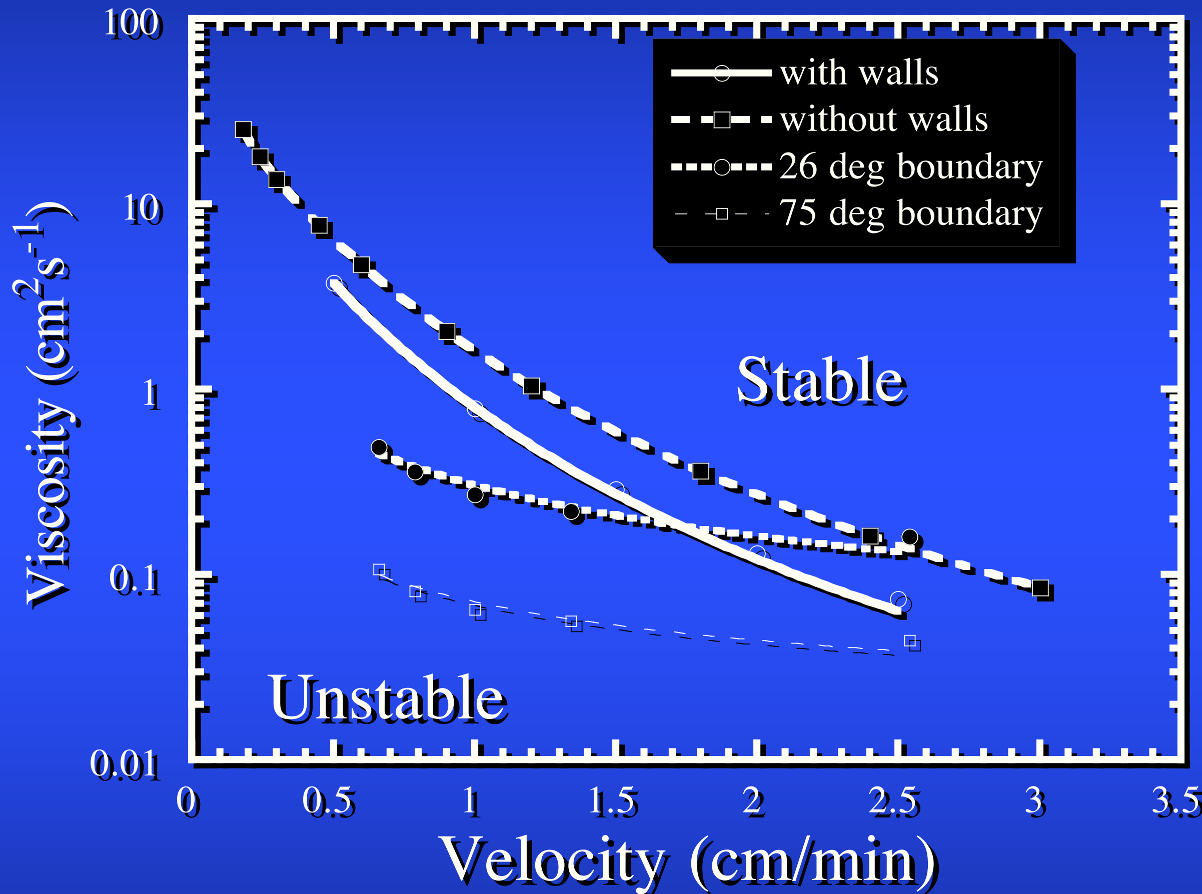


axisymmetric



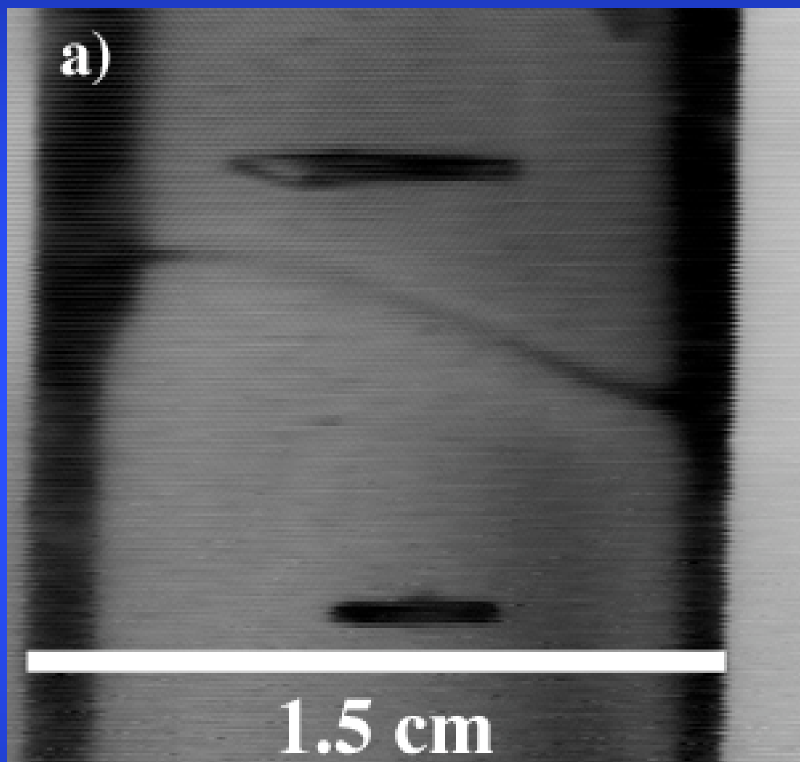
antisymmetric

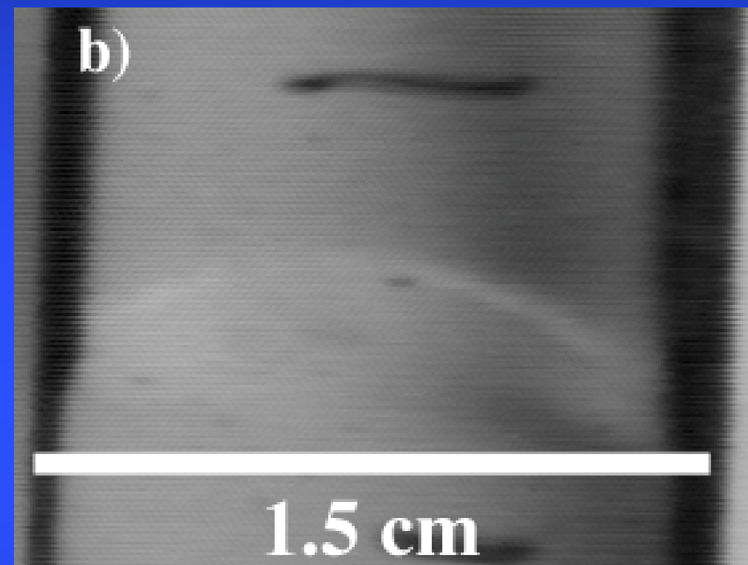
Linear Stability Analysis



Bowden, G.; Garbey, M.; Ilyashenko, V. M.; Pojman, J. A.; Solovyov, S.; Taik, A.; Volpert, V. "The Effect of Convection on a Propagating Front with a Solid Product: Comparison of Theory and Experiments," *J. Phys. Chem. B* **1997**, *101*, 678-686.

Liquid/Liquid Fronts





axisymmetric

antisymmetric

McCaughey, B.; Pojman, J. A.; Simmons, C.; Volpert, V. A. "The Effect of Convection on a Propagating Front with a Liquid Product: Comparison of Theory and Experiments," *Chaos* **1998**, *8*, 520-529.

Self-Propagating High Temperature Synthesis

NiAl gasless combustion

planar propagation

spin mode

Theory for One-Step Reaction

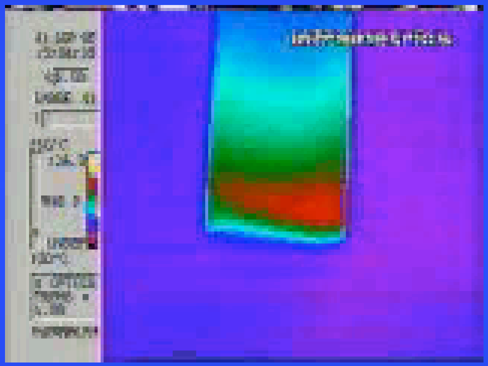
- stability determined by effective E_a, initial and front temperature (for adiabatic system)

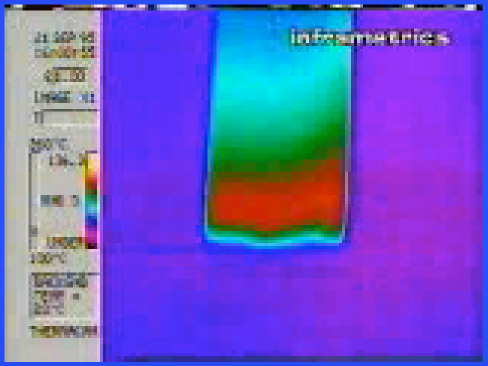
$$\alpha = \frac{E_a}{RT_{max}}\left(1 - \frac{T_0}{T_{max}}\right) < 8.4$$

Zeldovich Number

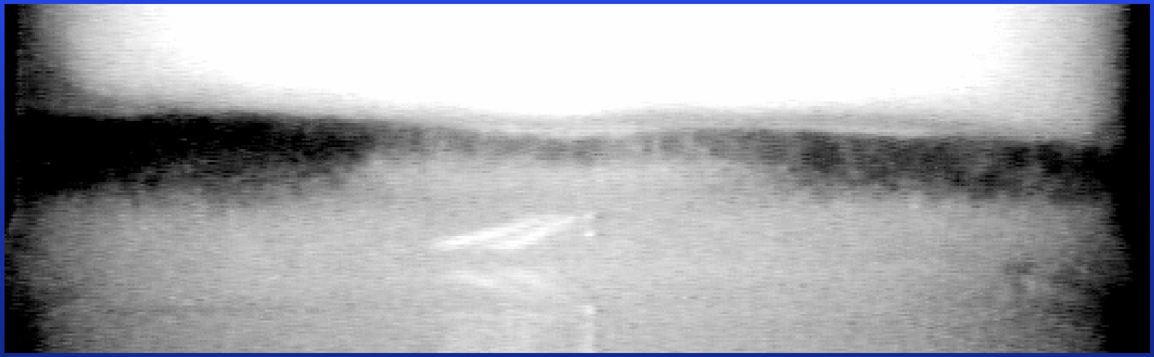
Spin Modes with Methacrylic Acid at $T_0 = 0$ °C

infrared

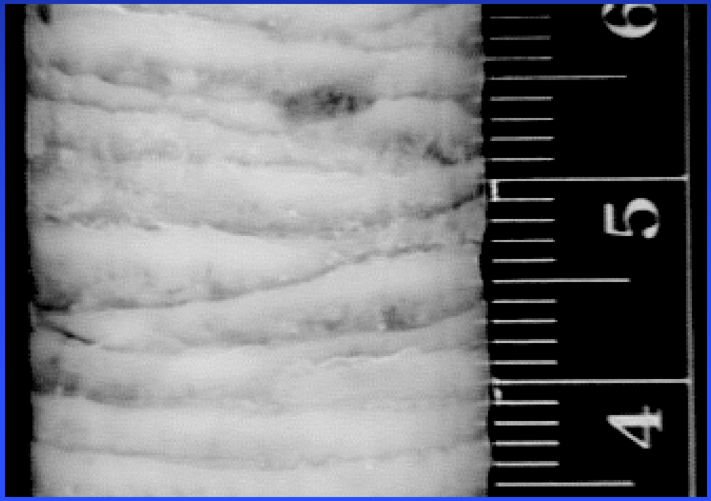




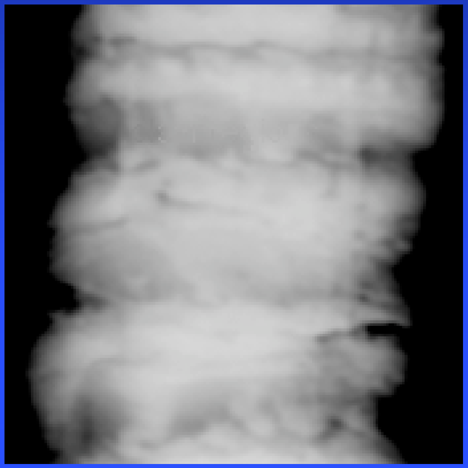
visible



Spiral Patterns



multiple head

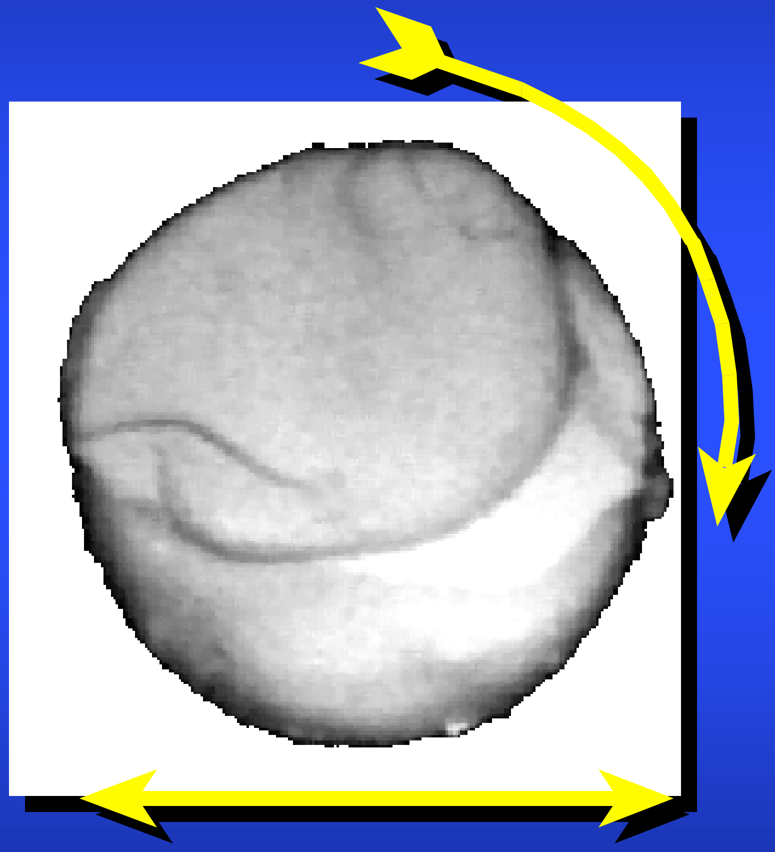


single head

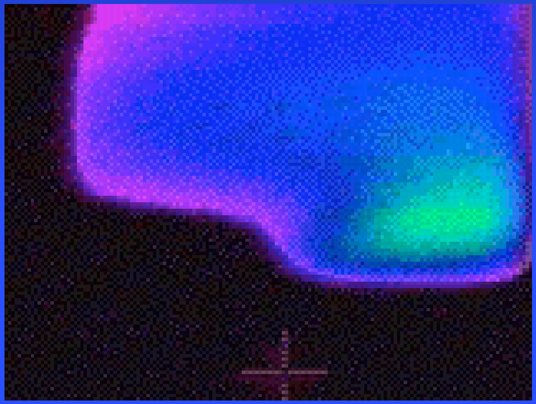
Mechanical and optical properties are degraded

Are there bifurcation sequences in the macroscopic properties?

Bottom View

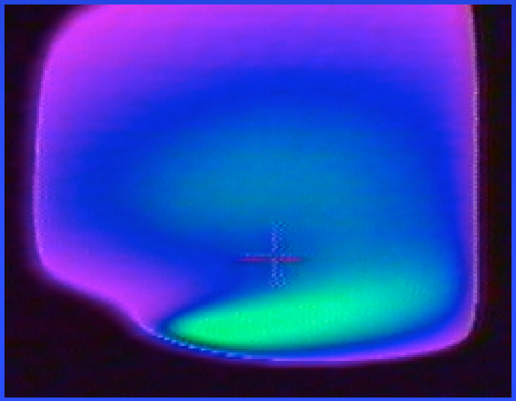


Fronts can propagate as a helix at room temperature

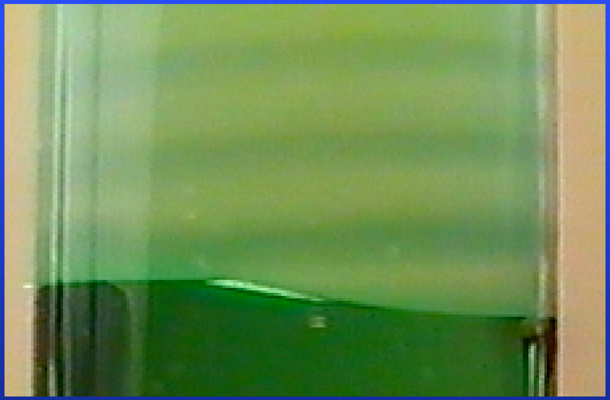


1.5 cm (i.d.) round

infrared imaging

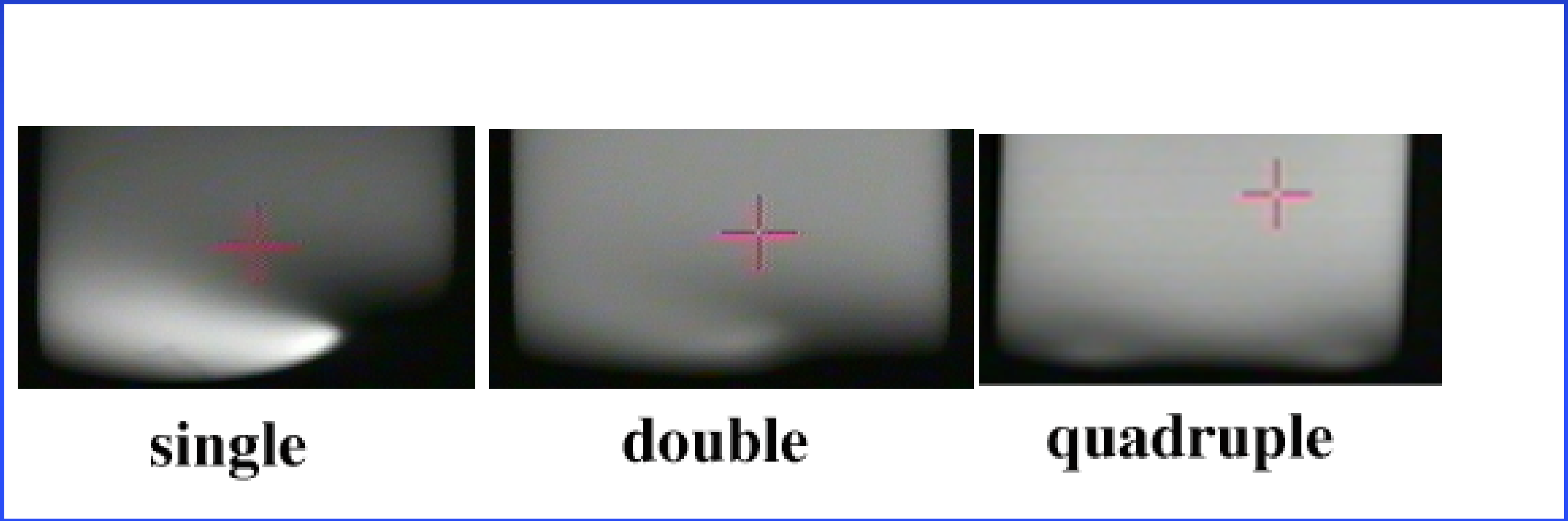


5X real time



visual

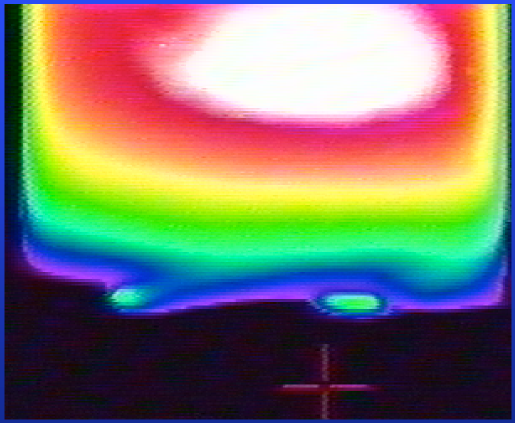
"Head-Doubling" Sequence



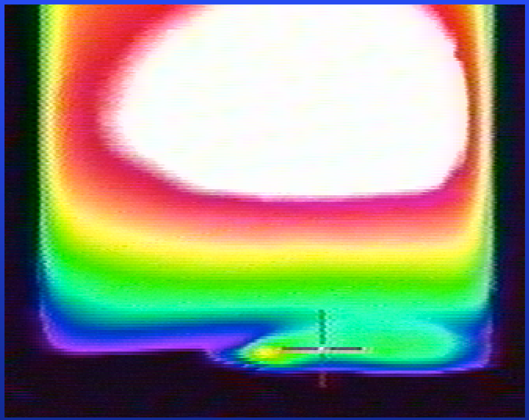
Increasing amount of trifunctional monomer

Bifurcation parameter is the ratio of trifunctional to monofunctional monomer.
Front temperature is unchanged.

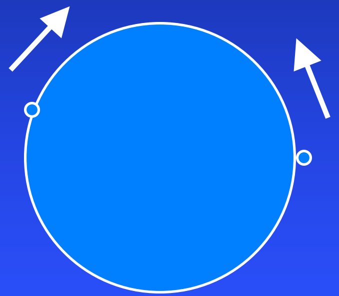
Complex Behavior

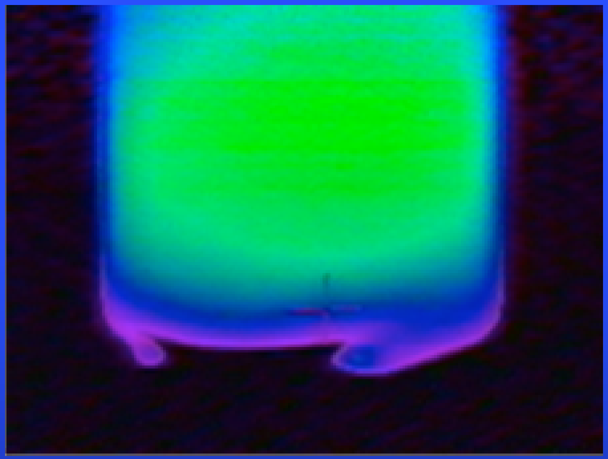


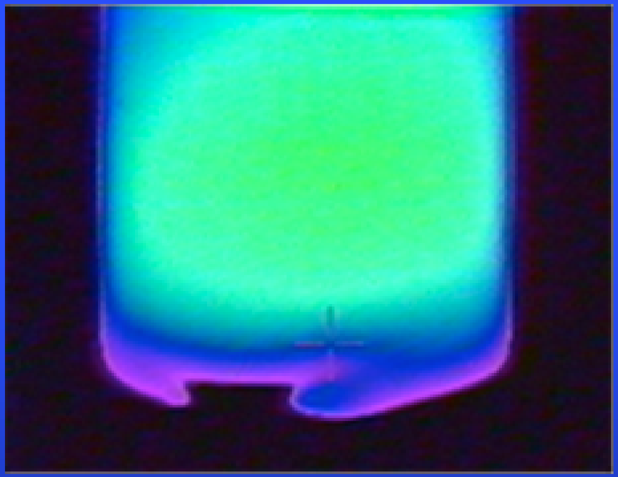
aperiodic



A New Mode

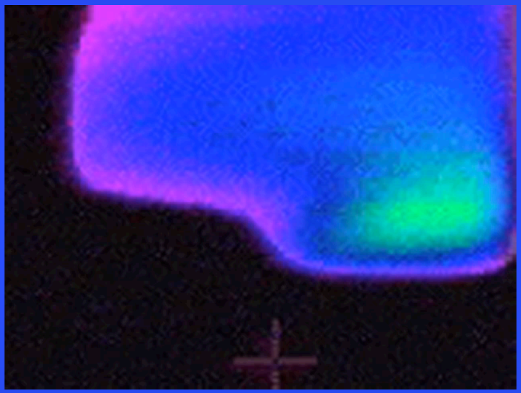




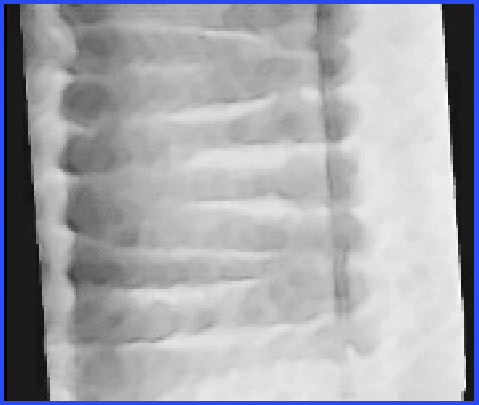


pulsating symmetric mode predicted by
Volpert et al. in 1992

Effect of Geometry: 4 Head



cylinder



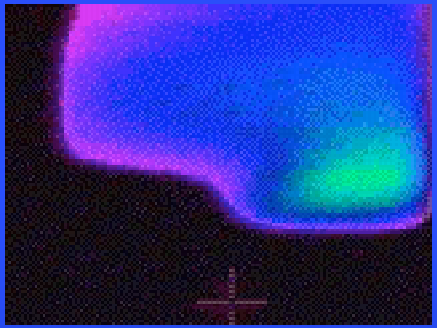
"Zig-zag" in square tube

Effect of Convection on Spin Modes

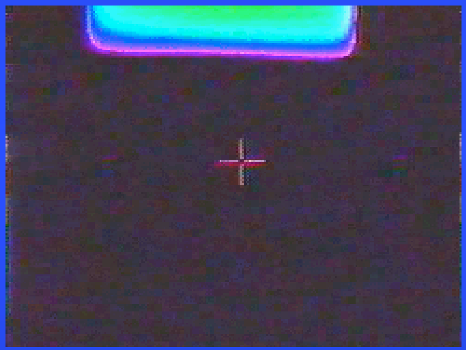
- solid front
  - ascending fronts are stabilized
  - descending fronts are destabilized
- liquid front
  - descending fronts are stabilized
  - ascending fronts are destabilized

predicted by Vitaly Volpert

Spin Modes disappear...



round

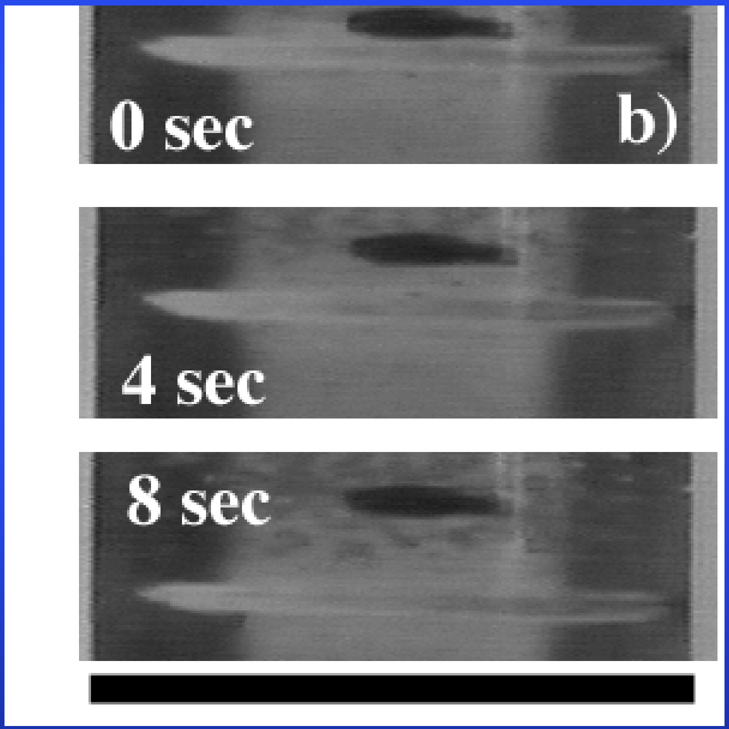


round

with high viscosity

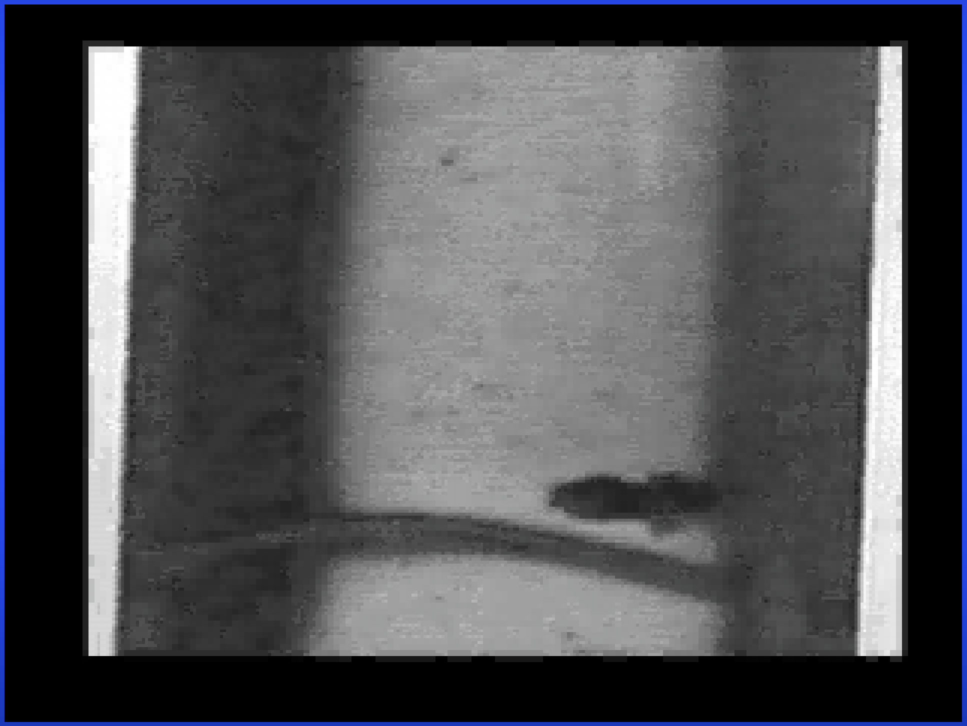
Liquid/Liquid Case

descending



no spin mode

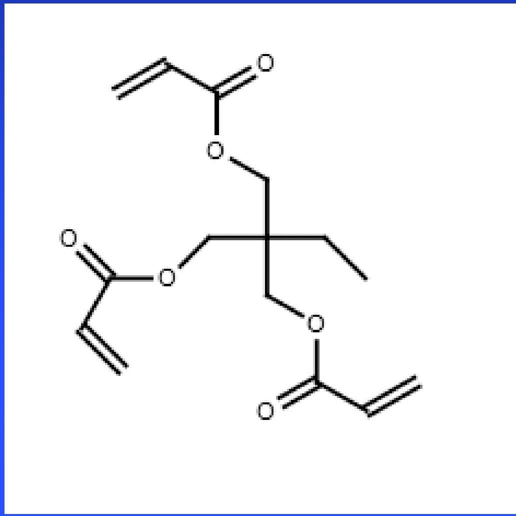
ascending



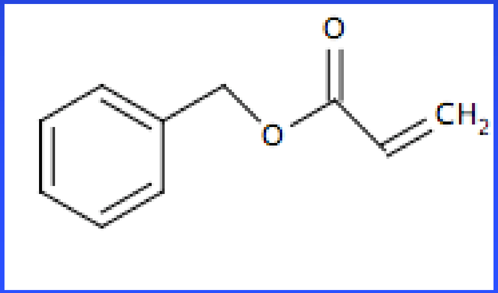
spin mode

5X real time

A little more polymer chemistry...



triacrylate

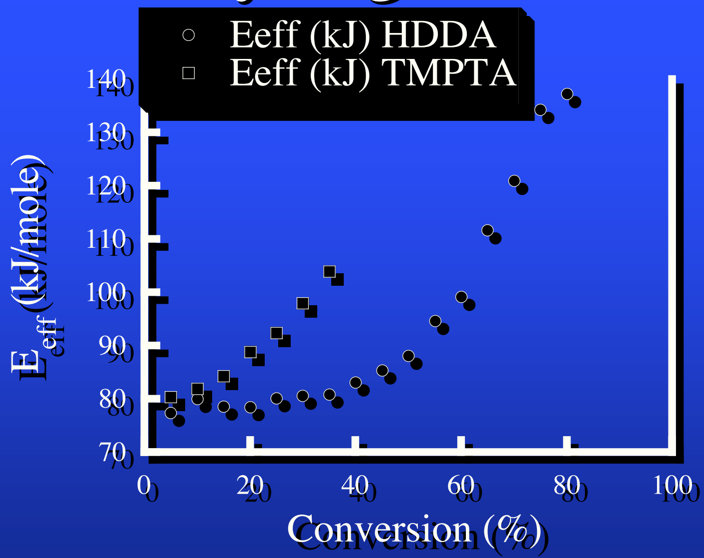


monoacrylate

A triacrylate forms a crosslinked network

Spin Modes at Room Temperature?

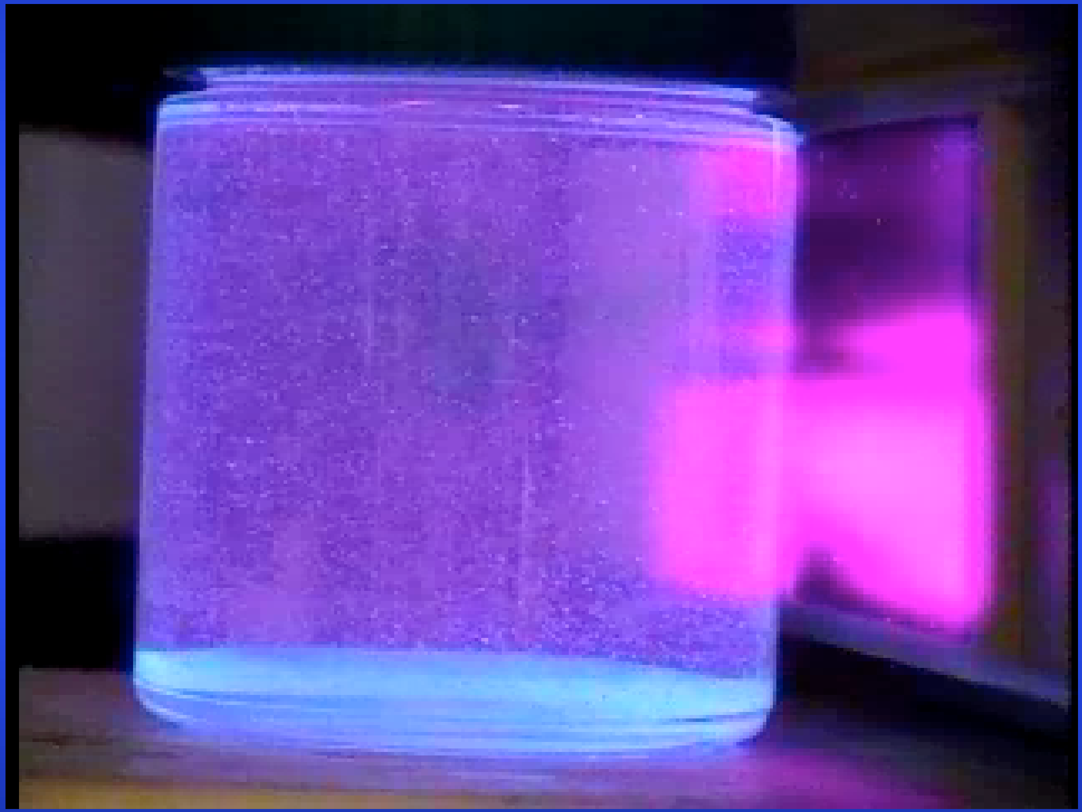
- energy of activation can be a function of conversion
- with crosslinked polymers, very high Ea at room temperature



Holy Grail for 16 years: Spherically-propagating front

- Viscous to avoid convection
- Bubble-free
- Support spin modes

Inside-out-curing



Diacrylate + silica gel + persulfate as bubble-free initiator

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PUBLISHED IN 2 PARTS
Articles published online in Wiley InterScience,
3 January 2006 through 23 January 2006
JOURNAL OF
POLYMER SCIENCE
Spherically Propagating Polymerization Fronts
0 s
8 cm
8 s
12 s
15 s
21 s
30 s
PART • A
Polymer Chemistry
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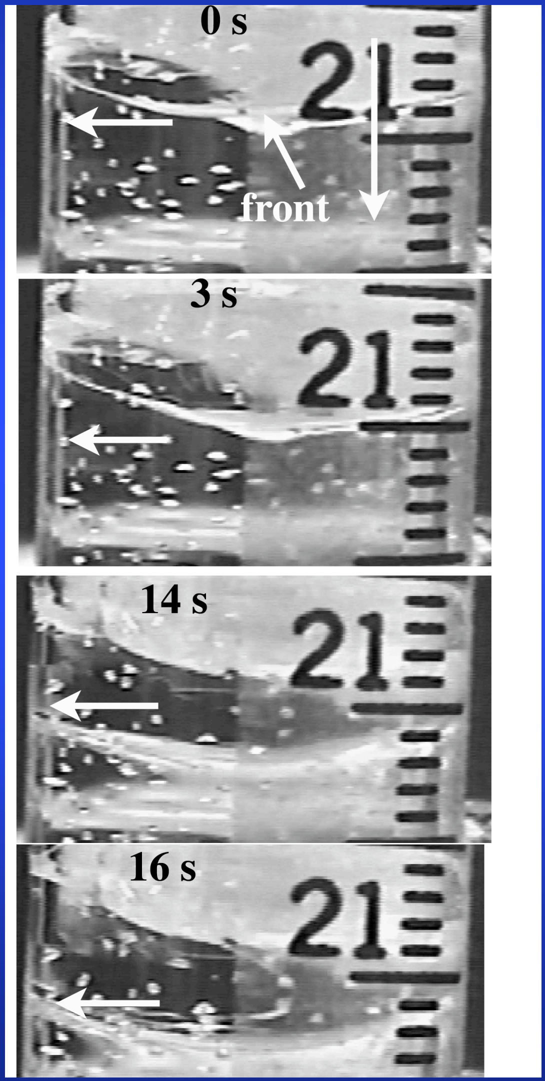
Developed ‘Spinning’ Gel System



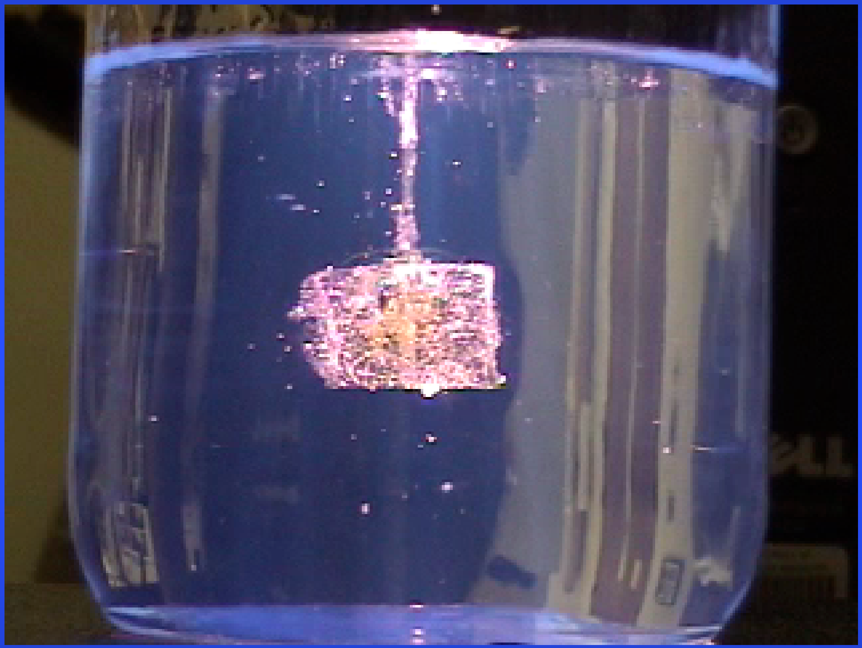
Gel formed from amine-catalyzed Michael addition of a trithiol to a triacrylate --2/3 of triacrylate remained unreacted.

Front propagated via a free-radical polymerization with a peroxide.

No bubbles because of gel.

8 cm

Square-initiating source



Challenge for FP

- To create a system with low rate of reaction at room temperature but very high rate of reaction at adiabatic reaction temperature
  - Need large $|\Delta H|$ AND large E_a
  - Free-radical systems work well because of large E_a of peroxides or nitriles

New Approach

- Physically separate the reactive components
- Use microencapsulation as the method
- Breaking of capsules provides the thermal activation.

FP in Spatially-Modulated Media

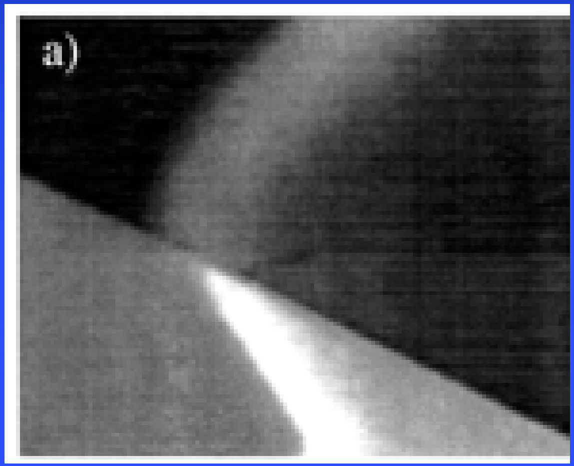
- Motivation:
  - Fillers will not always be uniformly distributed
  - Hole to be filled may be irregular
- Simplest case is bifurcated domain
  - Snell's law
- "Dick Cheney" experiment

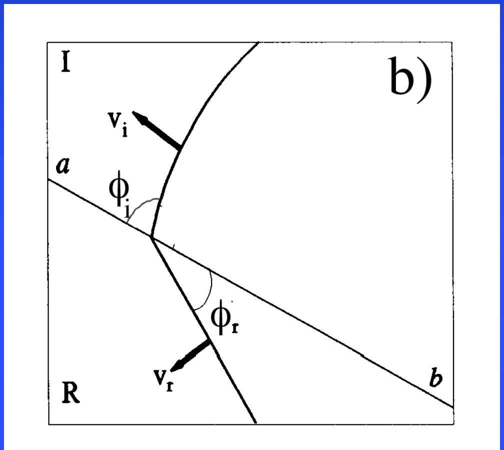
Snell's Law

Snell's law states that a front propagating at the interface of two regions in which the wave has a different velocity in each region will refract.

$$\sin \phi_i / \sin \phi_r = v_i / v_r$$

Snell's Law with BZ Waves

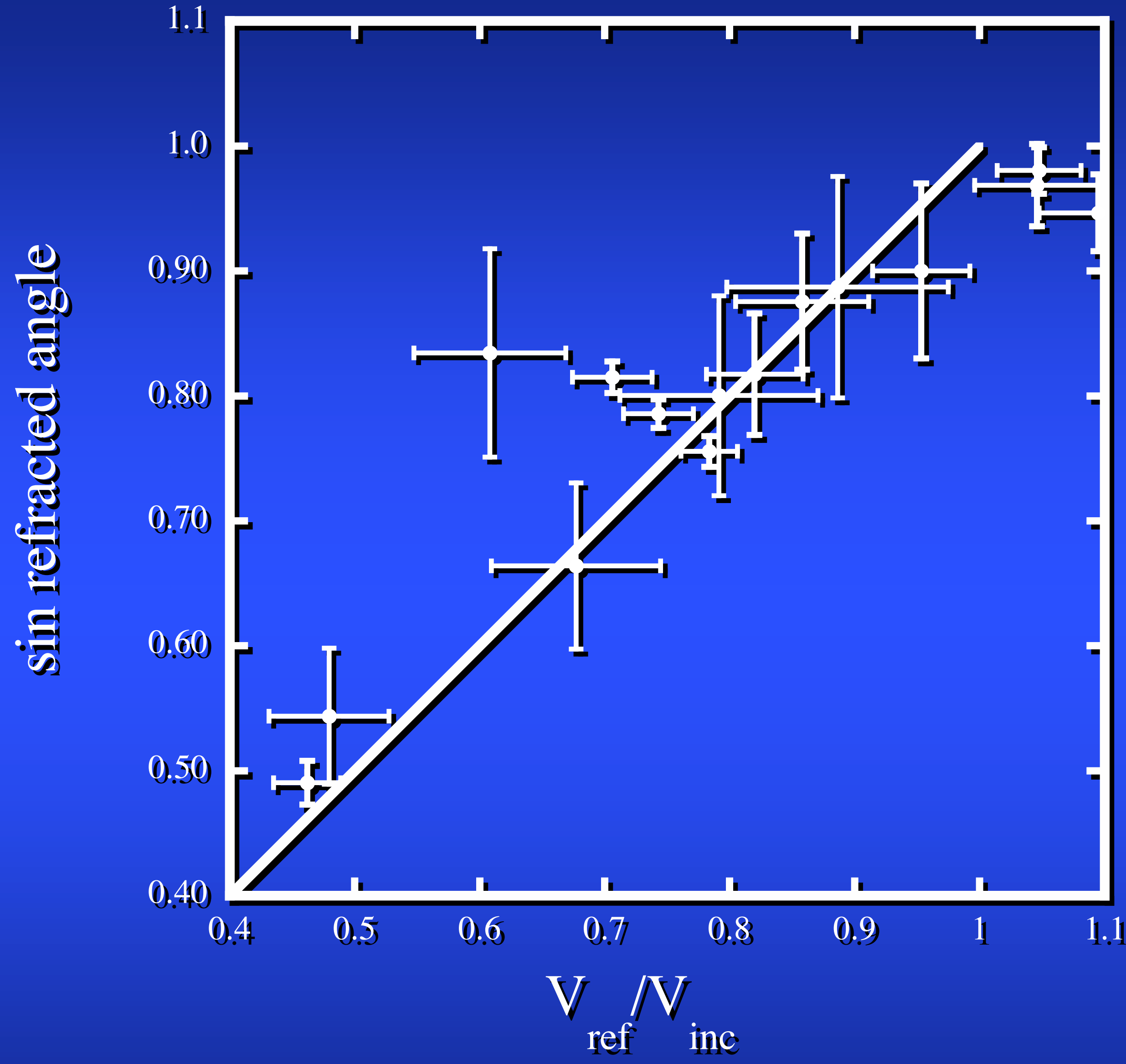




$$\frac{\sin \phi_i}{\sin \phi_r} = \frac{v_i}{v_r}$$

Zhabotinsky, A. M.; Eager, M. D.; Epstein, I. R.
Phys. Rev. Lett. 1993, 71, 1526-1529.


4%
1%



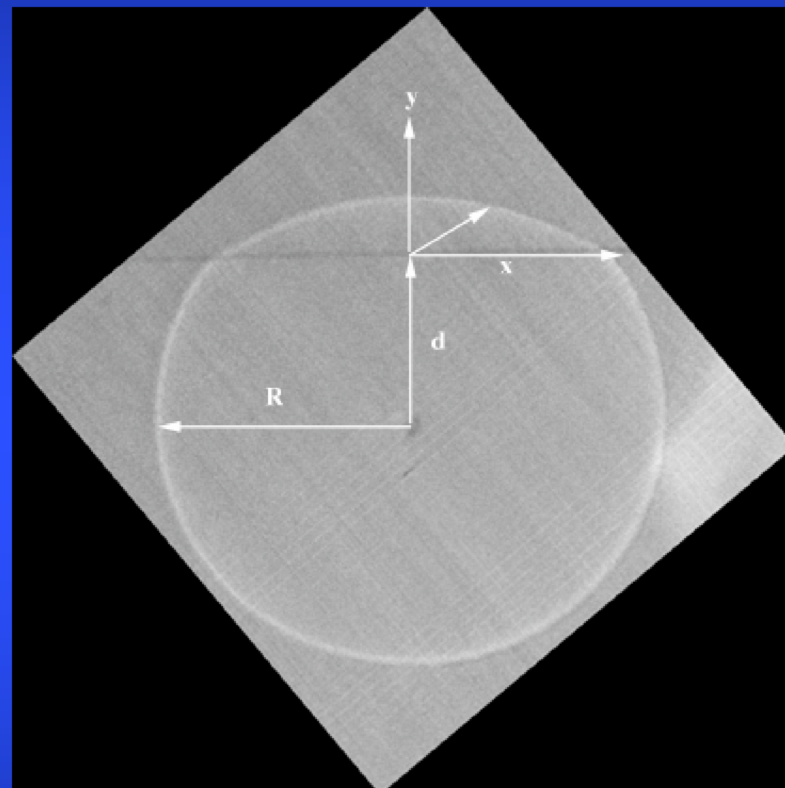
Pojman, J. A.; Viner, V.; Binici, B.; Lavergne, S.; Winsper, M.; Golovaty, D.; Gross, L. "Snell's Law of Refraction Observed in Thermal Frontal Polymerization," *Chaos* **2007**, *17*, 033125.

Method of Hwang & Halpin-Healy

$$x = [d(n^2 - 1)\tan\alpha + R\sin\alpha]/n^2,$$

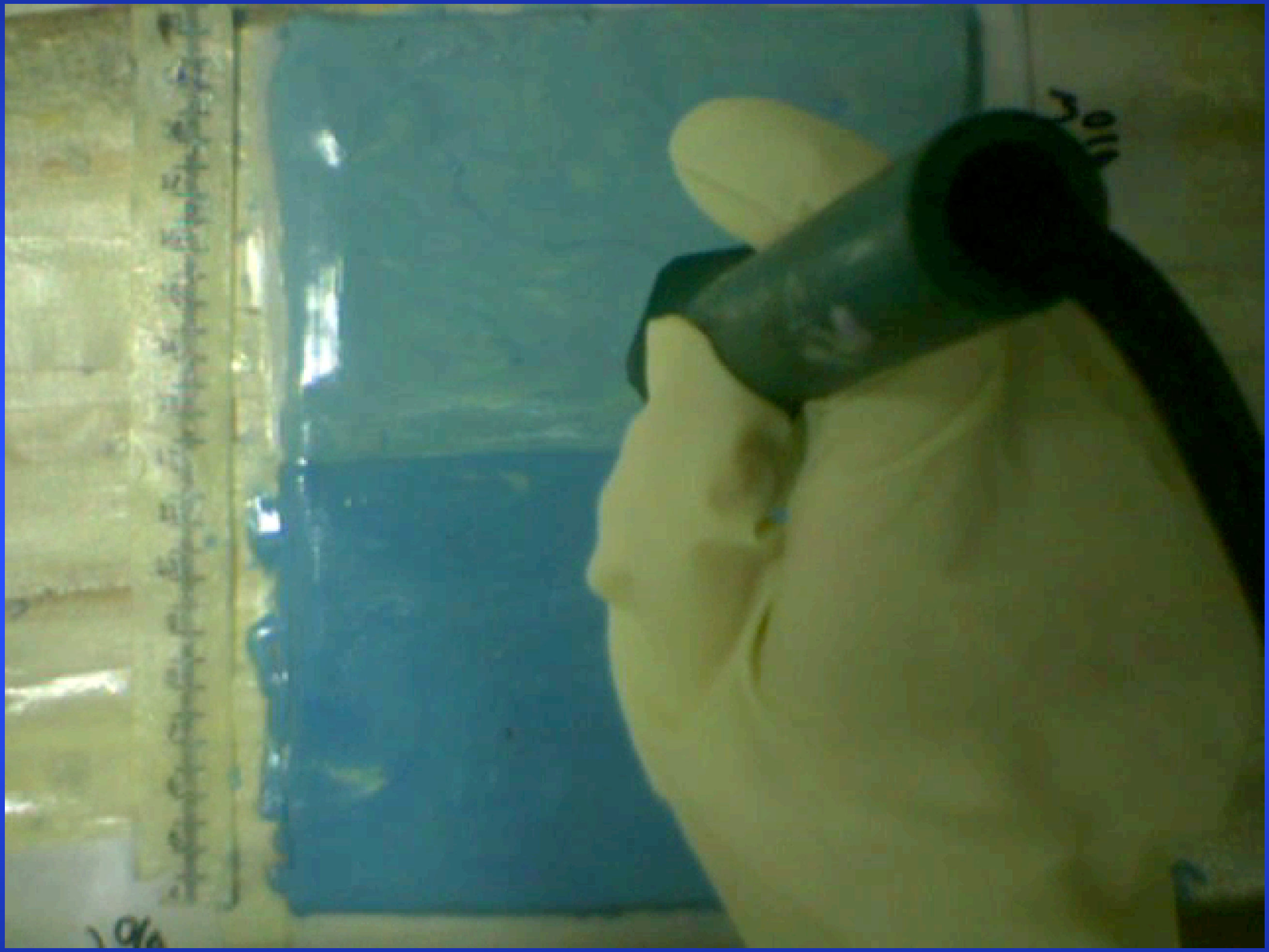
$$y = [(R - d\sec\alpha)\sqrt{n^2 - \sin^2\alpha}]/n^2,$$

$n = v_{incident}/v_{refracted} > 1$

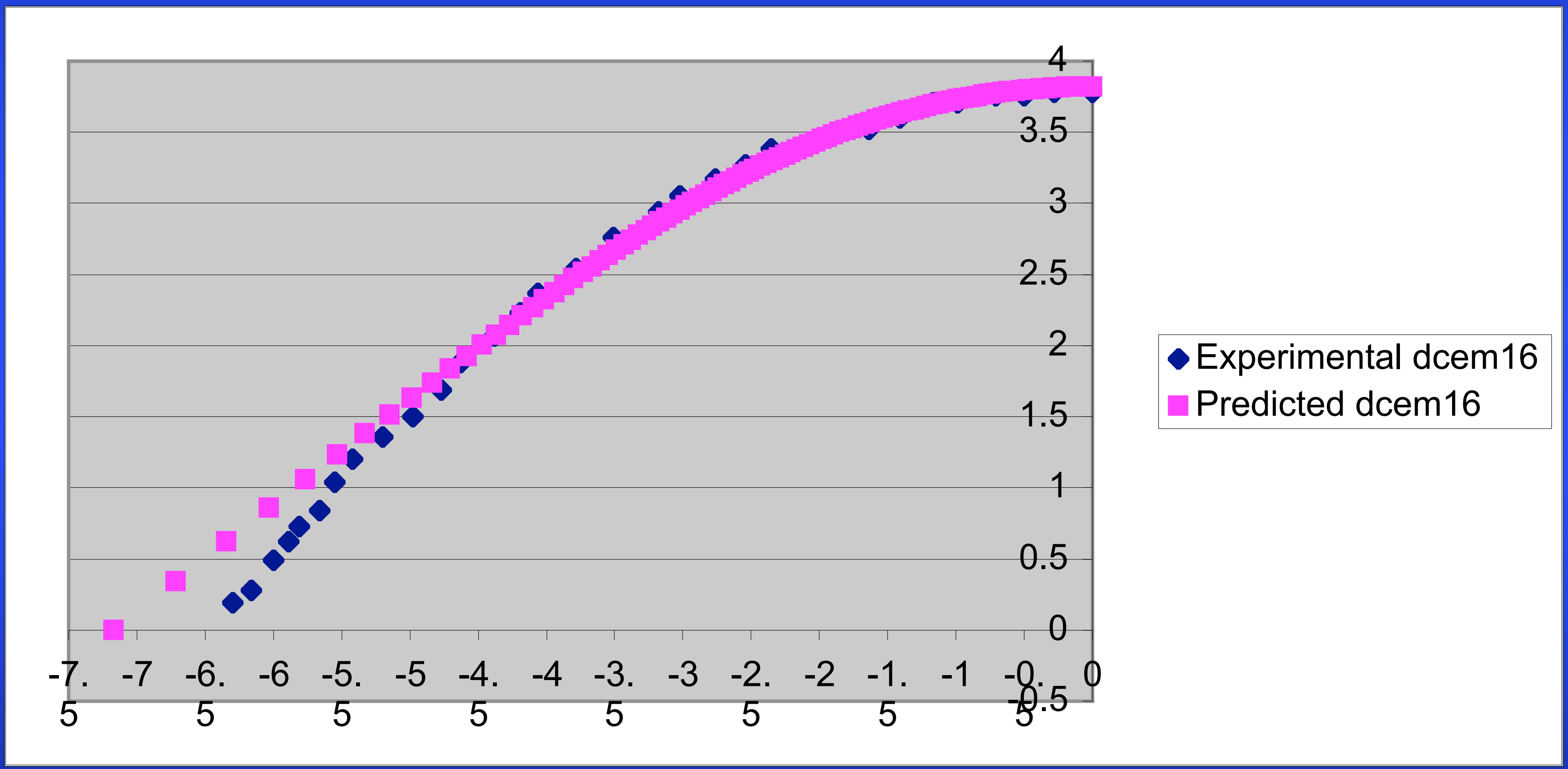


Hwang, S.-C.; Halpin-Healy, T. "Chemical Wave Refraction Phenomena," *Phys. Rev. E* **1996**, *54*, 3009-3012.

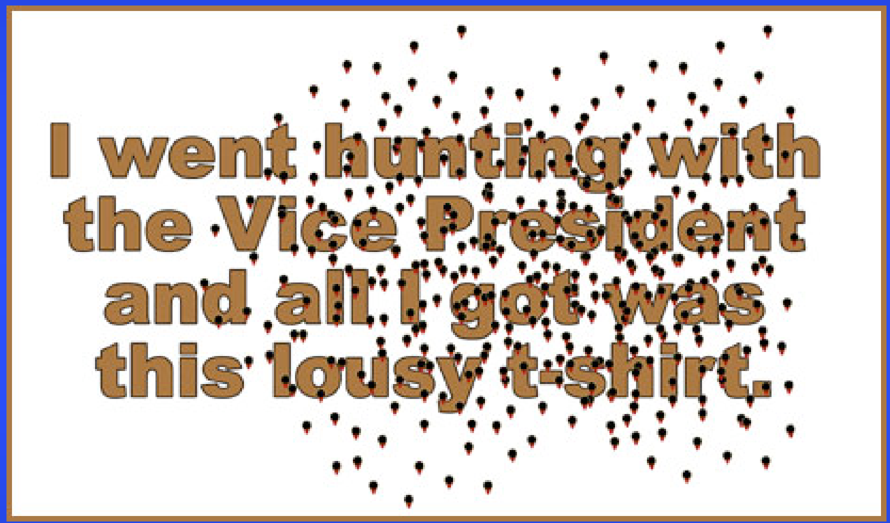
Fast to slow



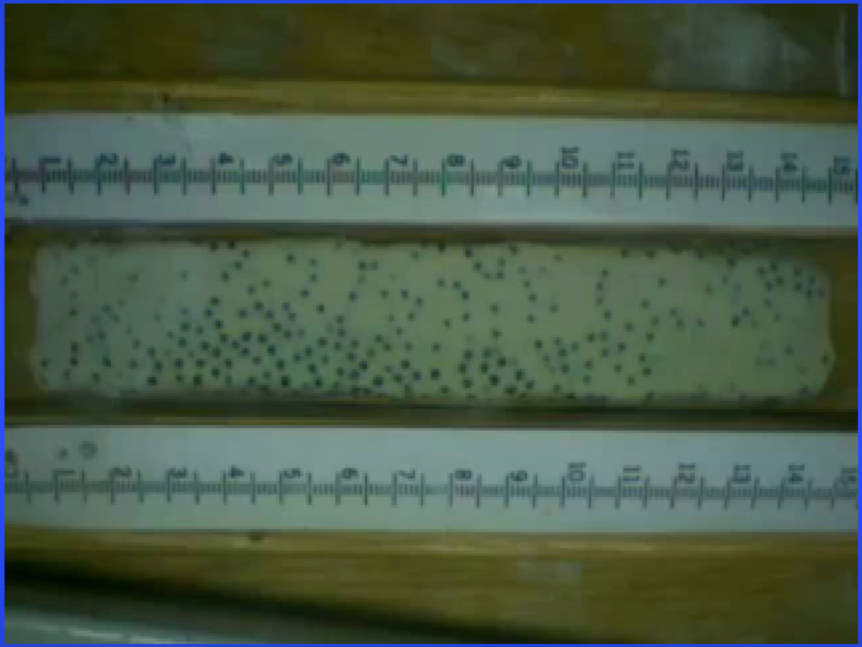
Reasonable Agreement



Dick Cheney Experiment

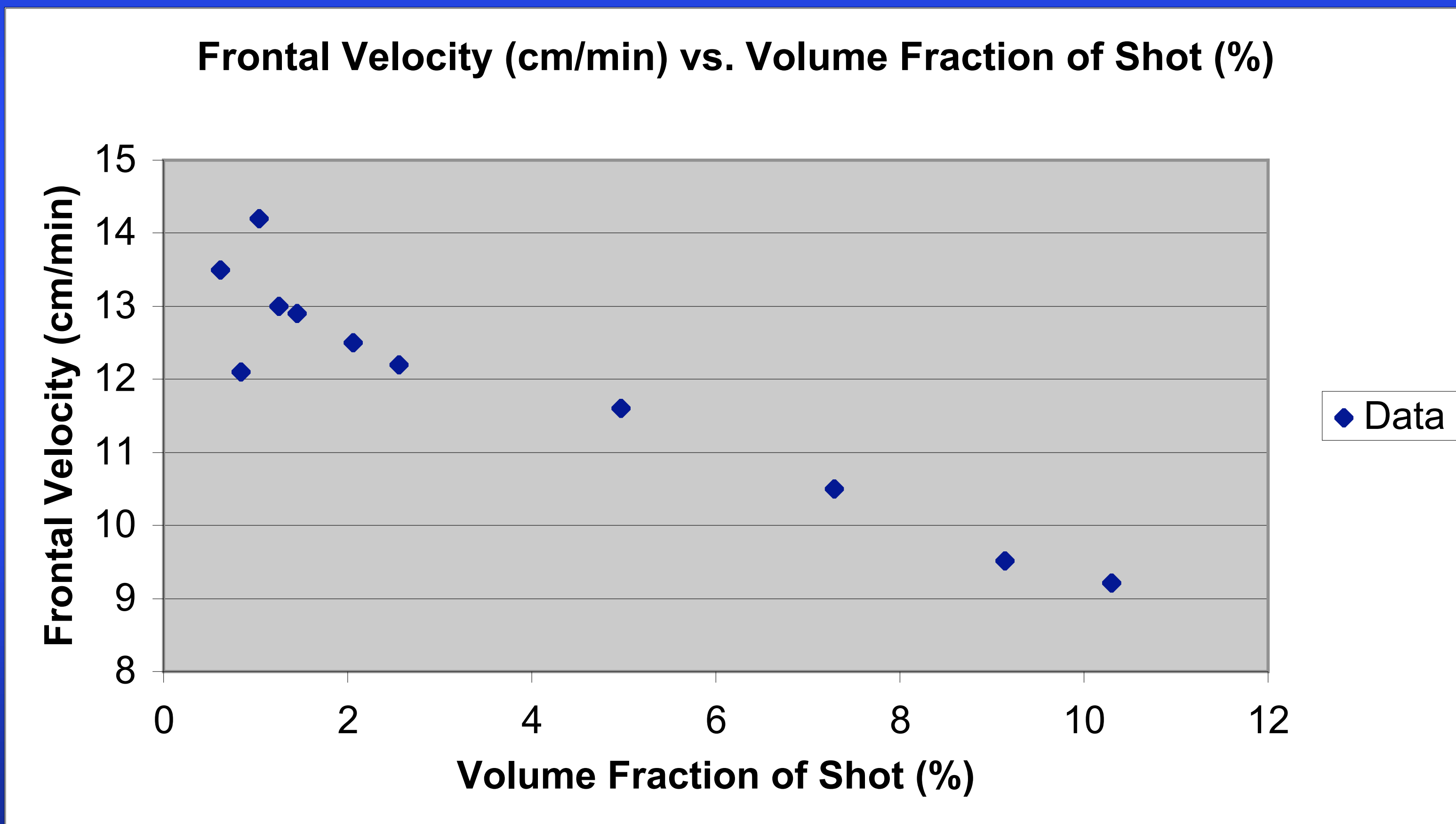


What if Vice President Cheney studied frontal polymerization?



7X real time

Triacrylate + clay + buckshot


Frontal Velocity (cm/min) vs. Volume Fraction of Shot (%)
Frontal Velocity (cm/min)
15
14
13
12
11
10
9
8
0
2
4
6
8
10
12
Volume Fraction of Shot (%)
Data

Current Challenges

- Eliminate smoking by lowering front temperature
- Front in thin layers

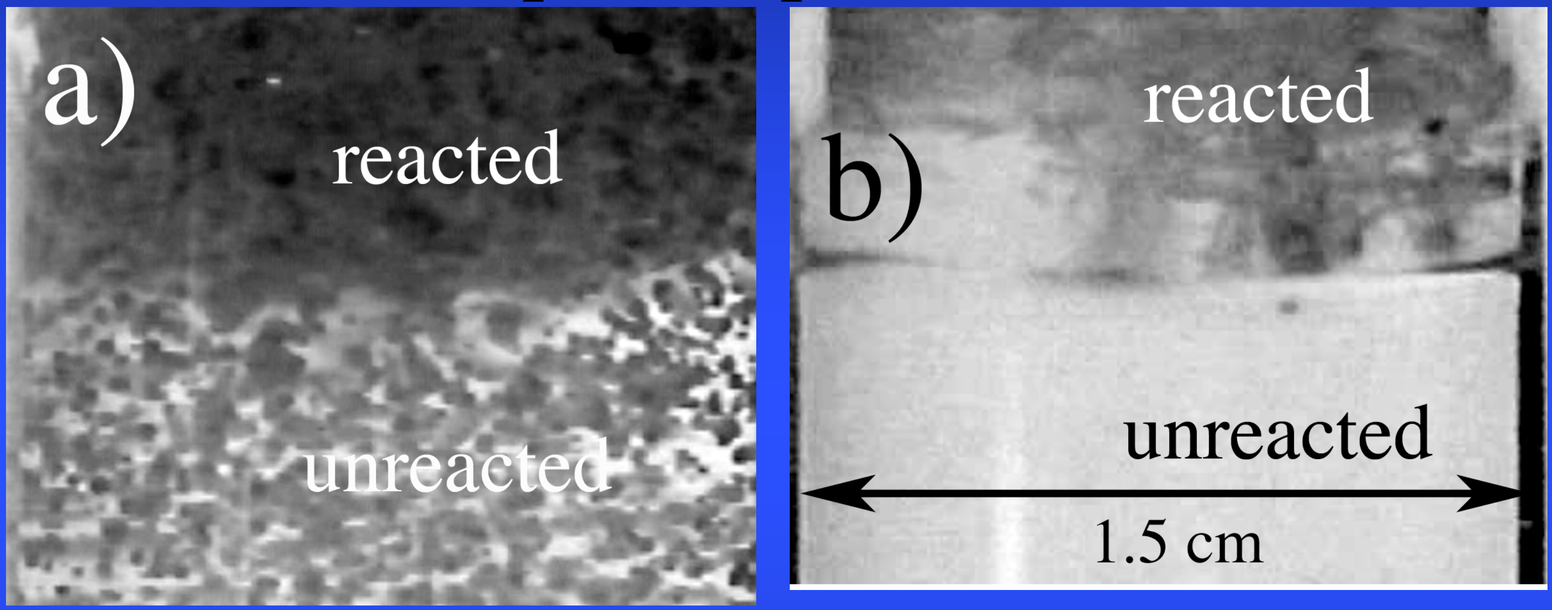
Challenge for FP

- To create a system with low rate of reaction at room temperature but very high rate of reaction at adiabatic reaction temperature
  - Need large $|\Delta H|$ AND large E_a
  - Free-radical systems work well because of large E_a of peroxides or nitriles

New Approach

- Physically separate the reactive components
- Use microencapsulation as the method
- Breaking of capsules provides the thermal activation.

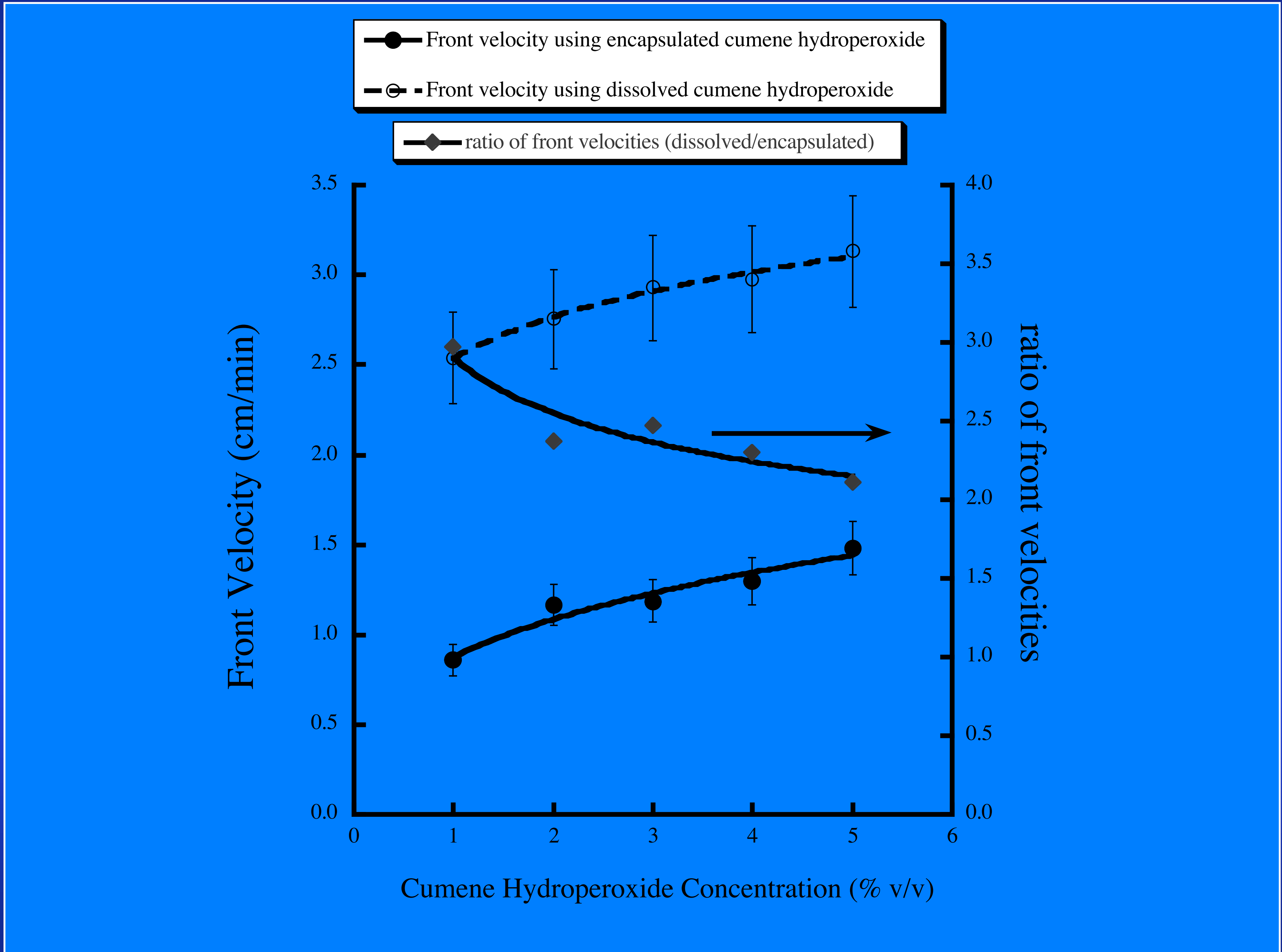
Microencapsulation of initiator (150 μ) for improved pot life



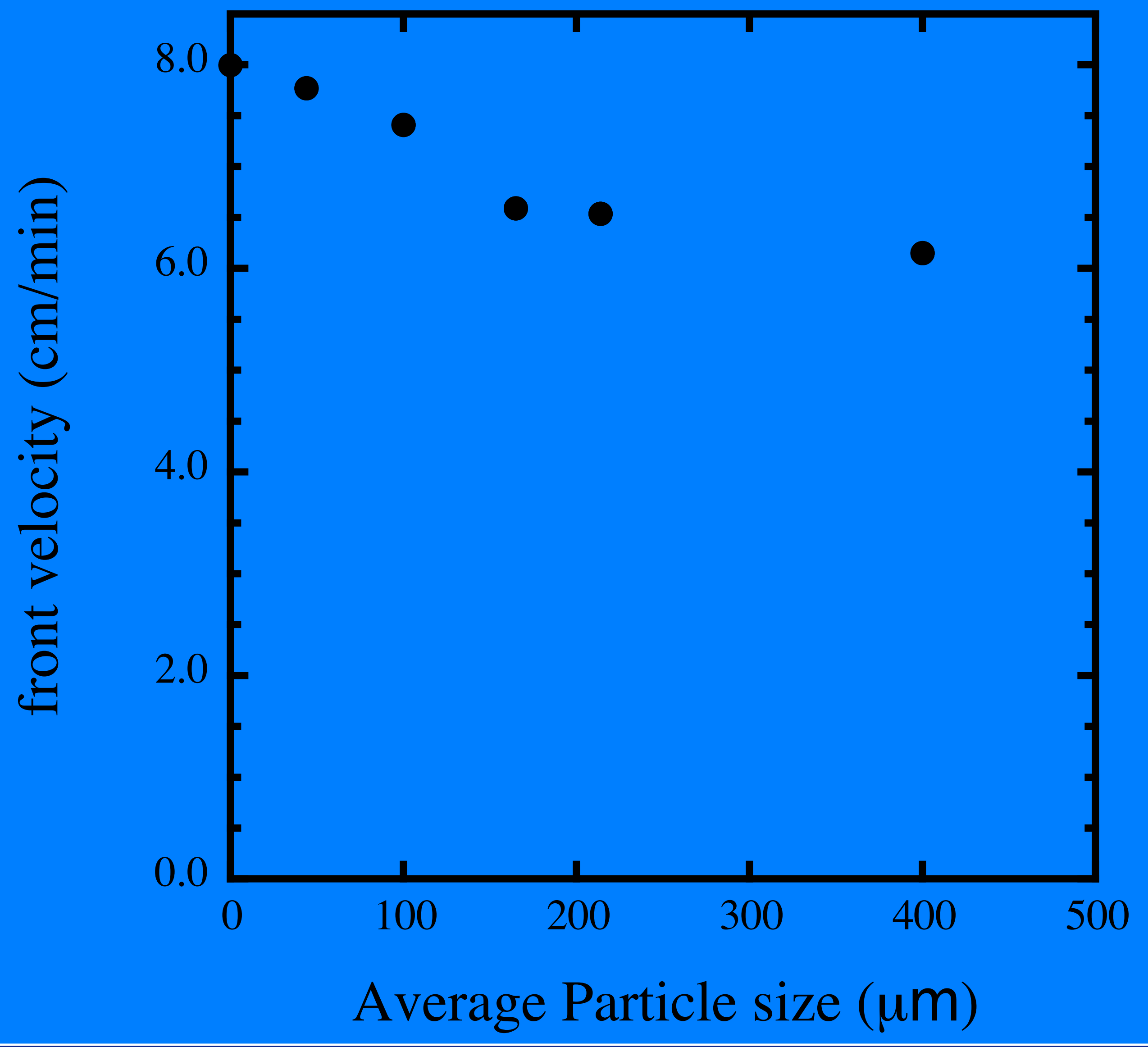
Encapsulated initiator

McFarland, B.; Popwell, S.; Pojman, J. A. "Free-Radical Frontal Polymerization with a Microencapsulated Initiator,"*Macromolecules* **2004**, *37,* 6670 - 6672.
McFarland, B.; Popwell, S.; Pojman, J. A. "Free-Radical Frontal Polymerization with a Microencapsulated Initiator: Characterization of Microcapsules and Their Effect on Pot Life, Front Velocity and Mechanical Properties," *Macromolecules* **2006**, *39,* 53-63.

J.A Pojman, B. McFarland, S. Popwell *Patent Pending*



Front velocity using encapsulated cumene hydroperoxide
Front velocity using dissolved cumene hydroperoxide
ratio of front velocities (dissolved/encapsulated)
Front Velocity (cm/min)
ratio of front velocities
Cumene Hydroperoxide Concentration (% v/v)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
0
1
2
3
4
5
6



front velocity (cm/min)
8.0
6.0
4.0
2.0
0.0
0
100
200
300
400
500
Average Particle size (μm)

Microencapsulated Diacrylate & Microencapsulated Initiator

Pack free-flowing powders and then ignite front

Patent pending

Effect of Encapsulated initiators

- The resulting polymer is **stronger** with encapsulated initiators than with dissolved initiators.
- NO spin modes.
- Not because of lower front temperature.

Open Questions

- What are the necessary conditions for frontal polymerization?
  - Enthalpy
  - Functionality
  - Ea for reaction
  - Reactor geometry
  - Filler loading
- What are the necessary conditions for initiation?
  - Light
  - Input of heat
- How are the frontal dynamics affected by changes in parameters during polymerization?
- How is stability affected by randomly-distributed components?

Practical Challenges

- Can frontal systems be prepared that propagate with temperature < 100 °C?
- Thin films?


Mississippi Catfish...
...not just for breakfast anymore