Fluorescence-Doped Particles for Simultaneous Temperature and Velocity Imaging

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Outline

- Review state of the art
- Technical approach
- Results at end of Phase I effort
- Results of Phase 2 effort
  - Laser Doppler Velocimetry (LDV)
  - Selection/Optimization of Kiton Red 620 (KR620)
  - Production of Large Batches
  - Particle Image Velocimetry (PIV)
- Next steps

Current state of the art

- Most common measurements in wind tunnels are lift, drag, force and moment
  - Also: surface pressure, surface heat transfer
- Off body, most common techniques:
  - Schlieren, non-quantitative flow vis
  - Laser Doppler velocimetry (LDV), u, v a … oint
  - Particle Image Velocim … v), u, v, w in a plane/volume

Easy to use, turn key, safe

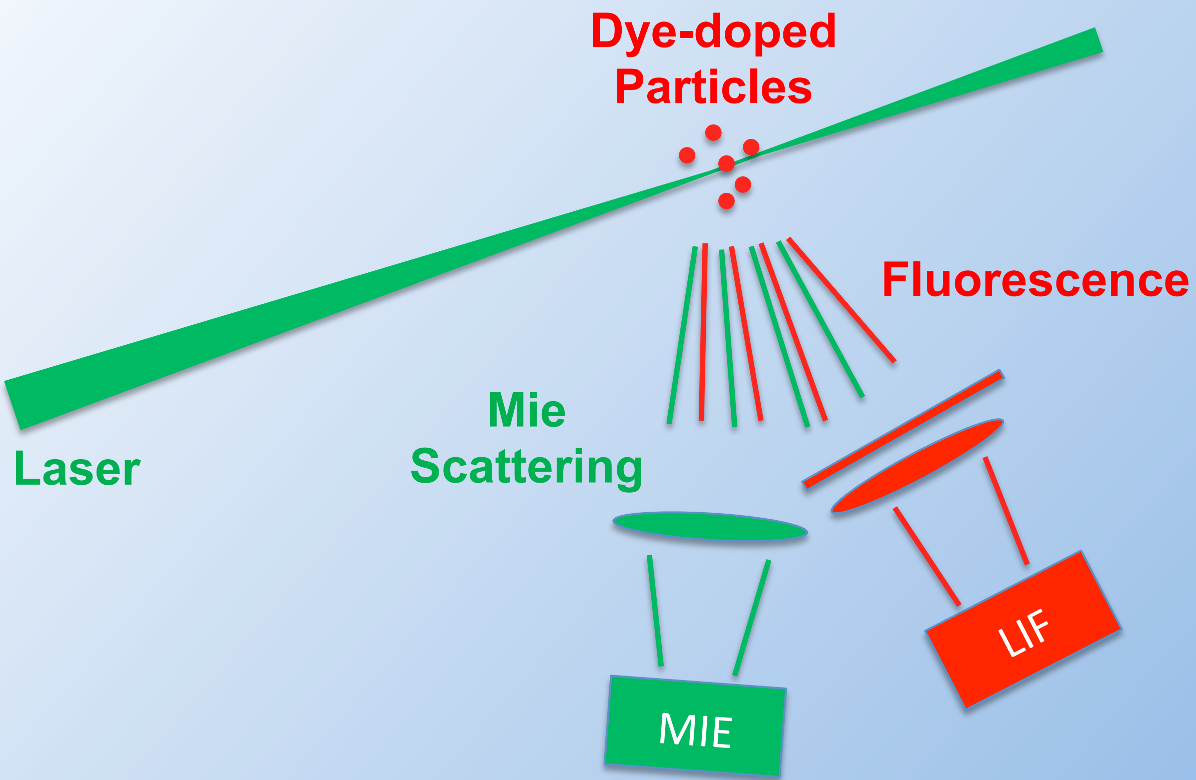
- Measurements not readily available:
  - In stream te … ure, concentration

Need: Easy to use, turn key, safe

Why Use Particles?

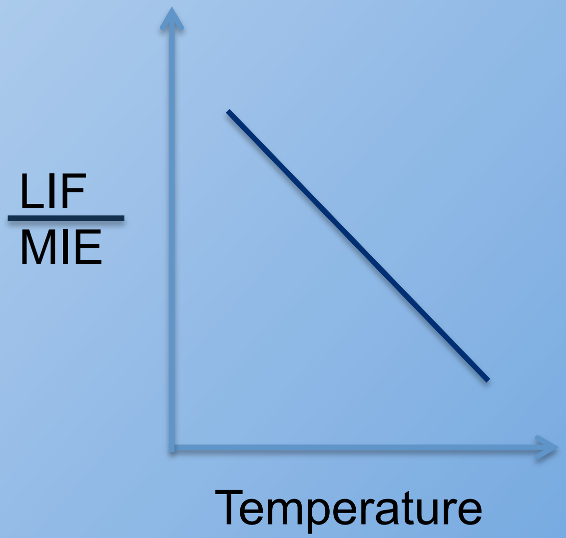
- Other ways of measuring flow temperature (without seeding particles) exist, but have limitations preventing their use:
  - CARS: complicated, expensive, hard to set up, single point, 10 Hz
  - Rayleigh/Raman scattering: low signal, complicated to analyze, often single point, 10 Hz
  - PLIF: must seed flow with (usually) toxic gas, complicated, not very accurate, not sensitive enough, 10 Hz
  - Thermocouple: intrusive probe, single point, slow time response
- Few or no viable methods of measuring flow pressure exist
- Seeding dye-doped particles into a flow to measure *T*, *P*, and/or stream concentration should allow high s/n images
  - Easy because uses same or similar lasers, seeding systems, detectors as PIV/LDV → prefer imaging, non-toxic seeding
  - Performing in conjunction with PIV/LDV will measure multi-parameters
  - Others have accomplished this, but with toxic seeds: we need safe seed.

Technical Approach: Measure T



Temperature (only) Measurement Approach

If dye has T dependence…



Technical Approach: Combine w' LDV

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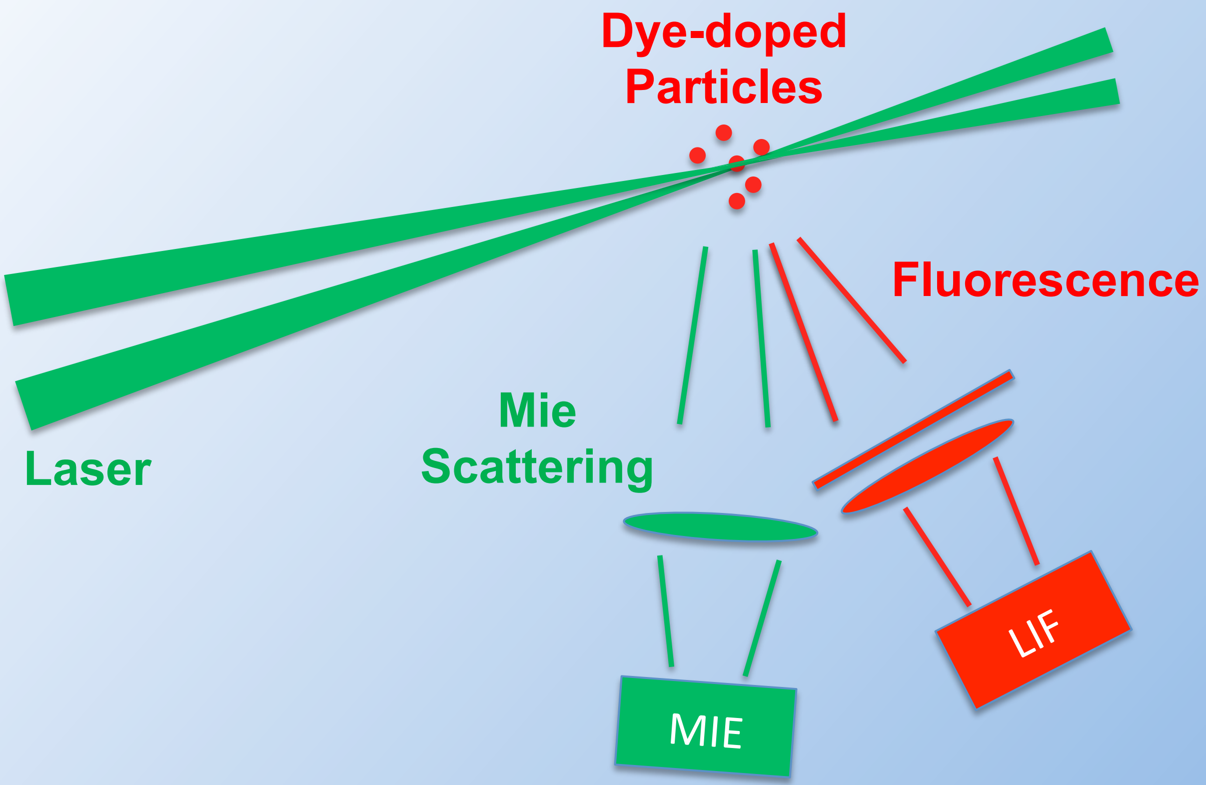
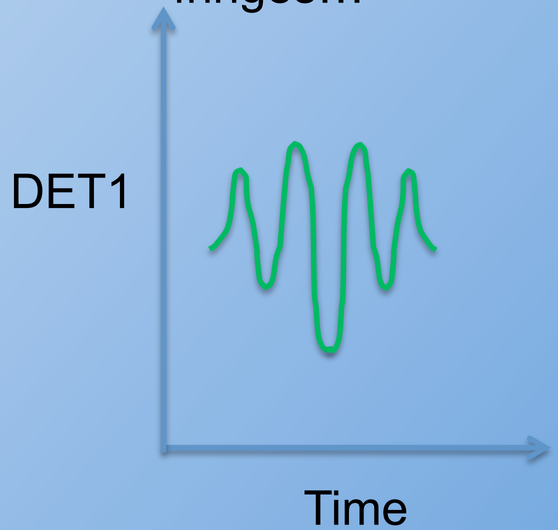


Measure velocity from frequency of collected light from particle passing through fringes…



Measure velocity from LDV, Temperature from fluorescence
Or: T and V from fluorescence (would allow measurement closer to surfae)

Technical Approach: Spectral Shift / Imaging

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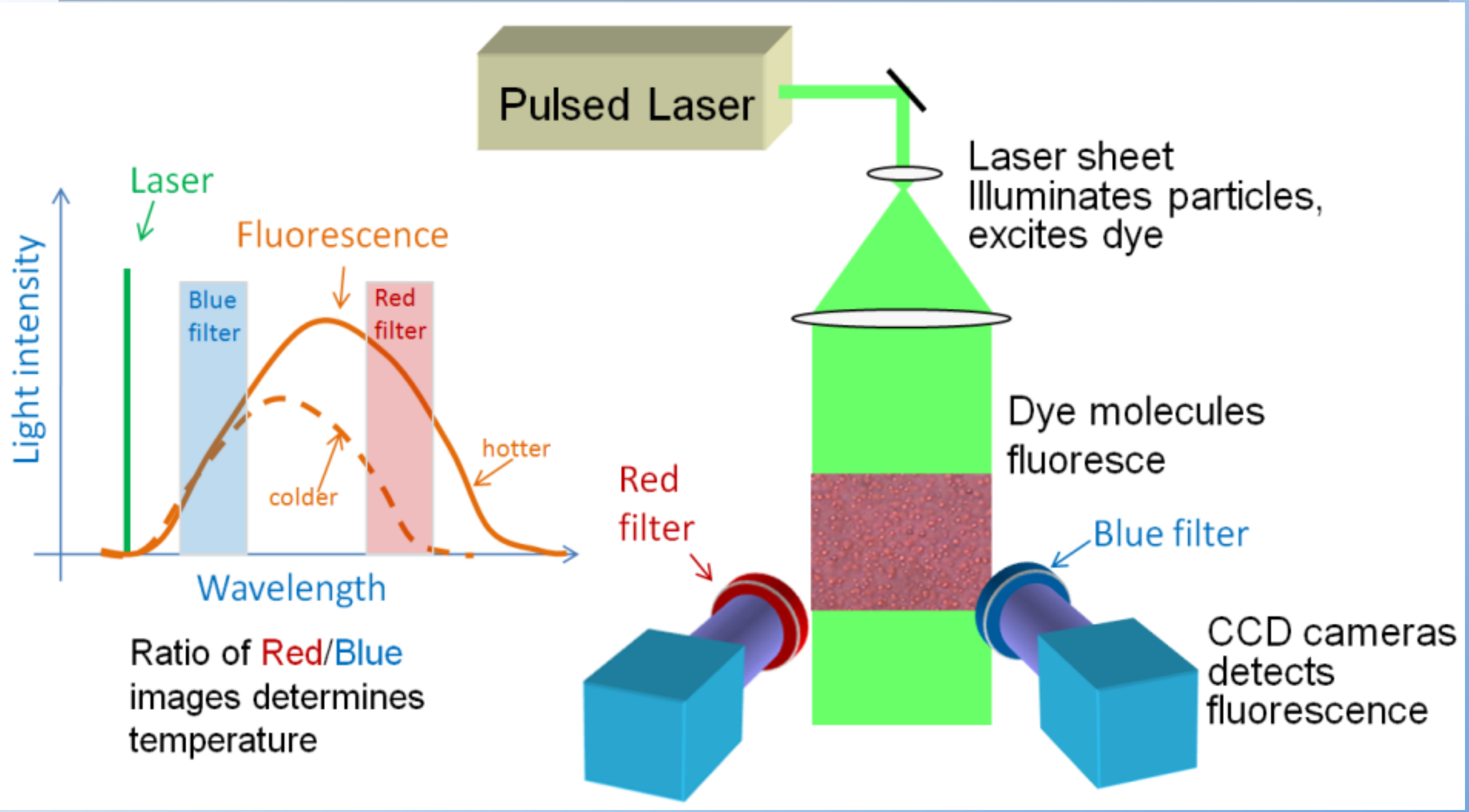
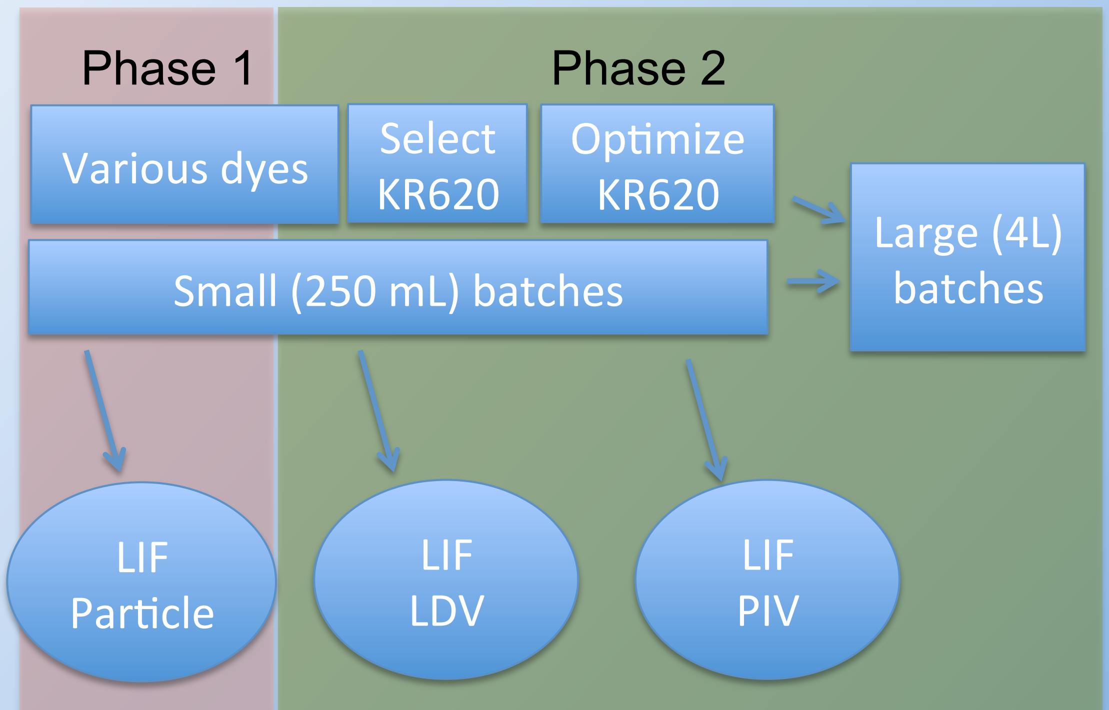


Combine temperature measurement with Particle Image Velocimetry (PIV)
Can use same spectral approach for laser Doppler velocimetry (LDV): self reference

Graph of Project Progress



PSL Particle Production

- Prior to project, we produced polystyrene latex (PSL) spheres for wind tunnel tests
  - Soap-Free Emulsion Polymerization
  - 1 micron spheres for LDV, PIV
  - Had produced Rhodamine B doped PSLs but safety concerns; no spectral shift with temperature
- Wished to dope *safer* dyes into PSLs
  - Large LIF intensity
  - Narrow particle size distribution
  - No leaching of dyes
  - Temperature sensitivity

Health	2
Fire	1
Reactivity	0
Personal Protection	E

Soap – Free Emulsion Polymerization

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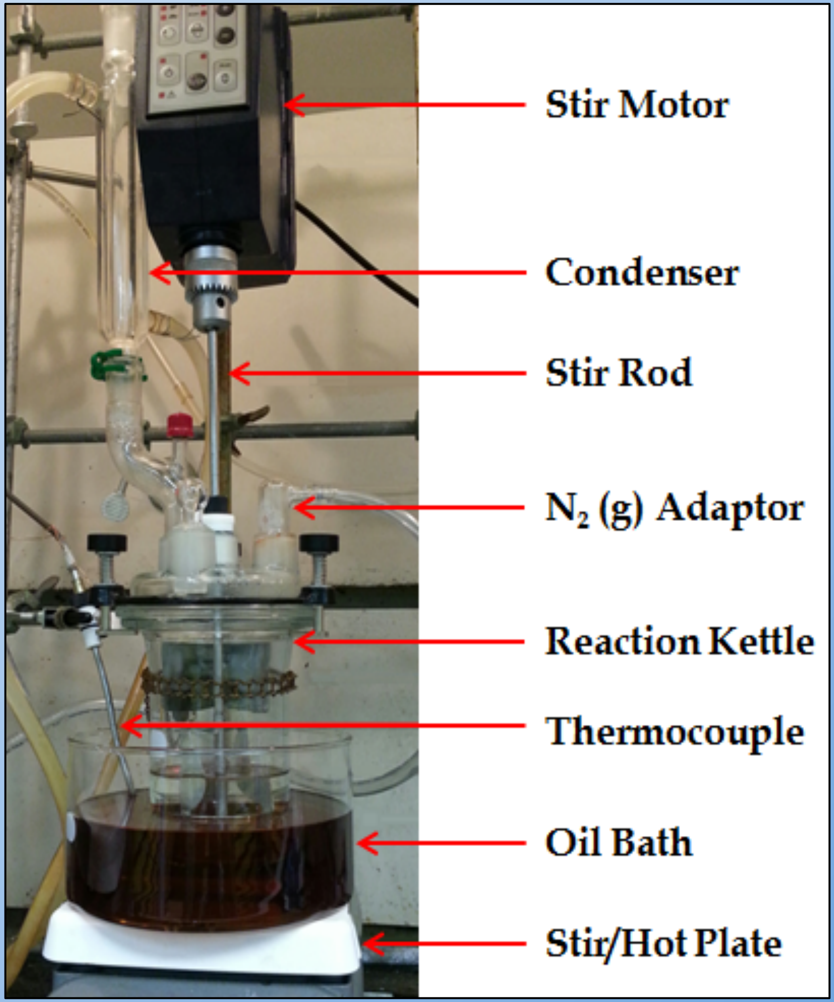
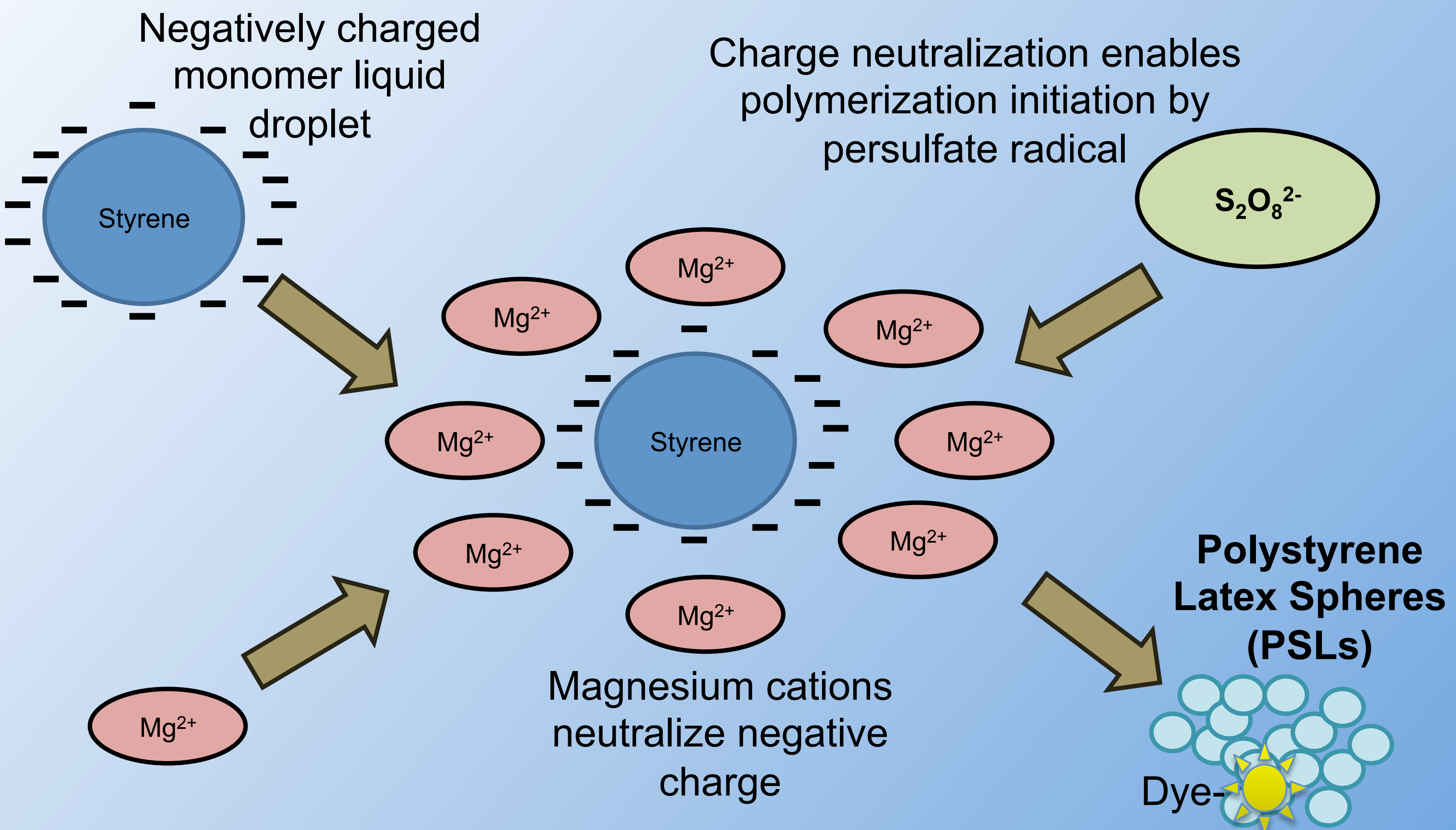
- Mixing of monomer in aqueous solvent creates emulsion of styrene droplets
- Conventional method uses surfactant to stabilize monomer droplets and developing particles
- Soap-free process uses an electrolyte for ionic stabilization
- Added dye gives fluorescence to particles

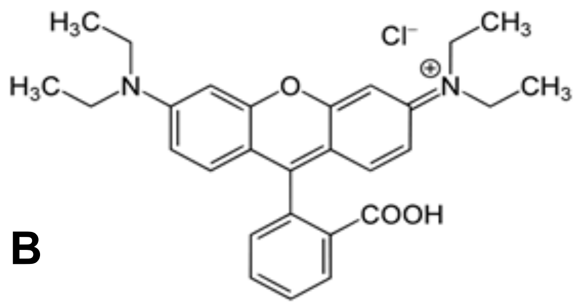


Technical Approach: PSLs

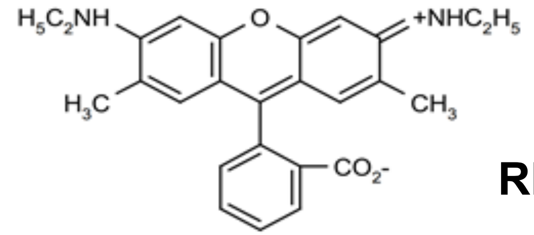


How do we attach the dye?

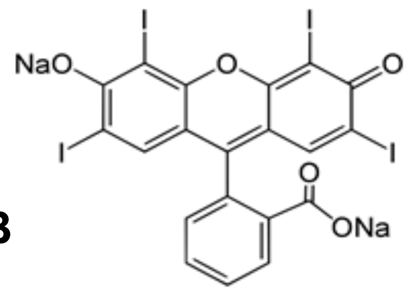
Candidate Dyes



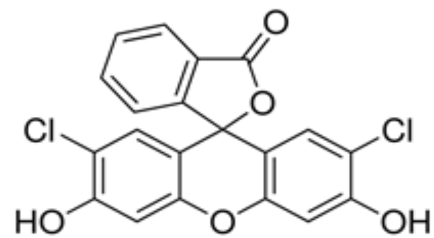
Rhodamine B



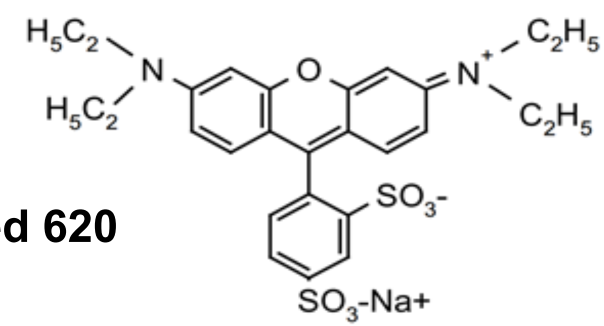
Rhodamine 575



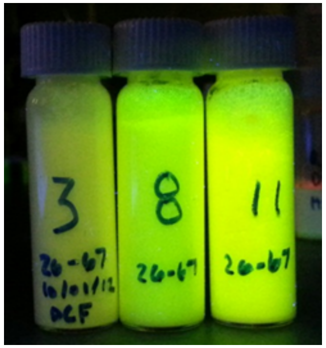
Erythrosine B



Dichlorofluorescein



Kiton Red 620



Effect of pH

Selection of Kiton Red as Dye

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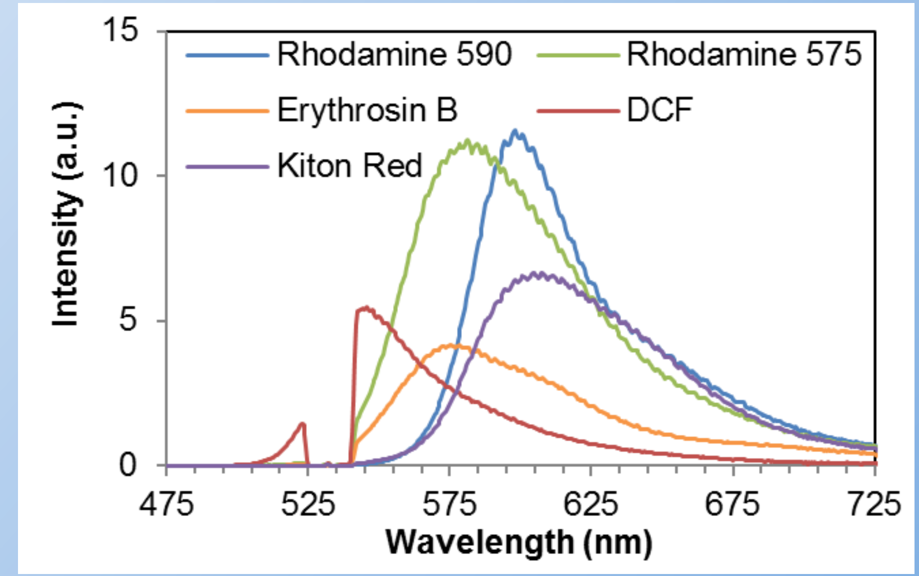
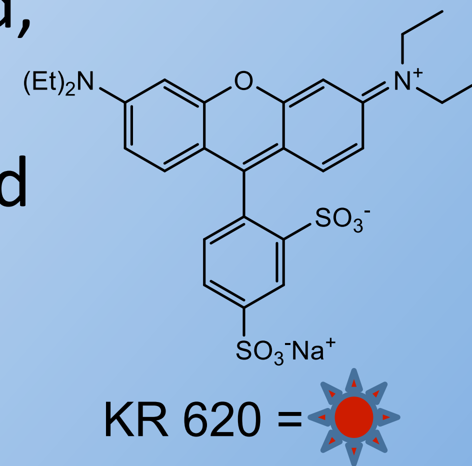
- Various dyes were successfully incorporated into PSLs during synthesis, but had undesirable attributes
  - Rhodamine Family (carcinogenic, toxic)
  - Dichlorofluorescein (not reproducable)
- Past research suggested Kiton Red 620 as a potential dye
  - Spectral properties
  - Temperature response
  - Lower health risks
  - Reproducible

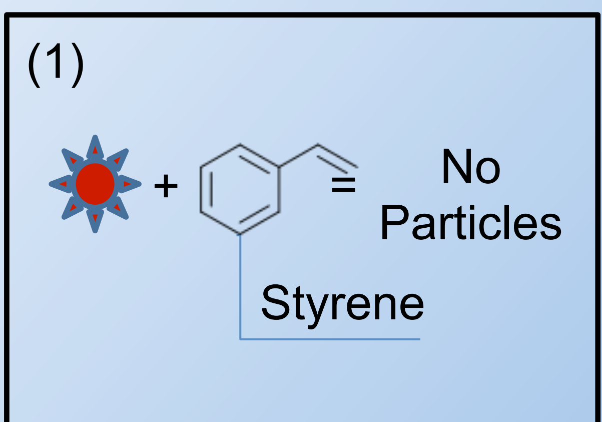


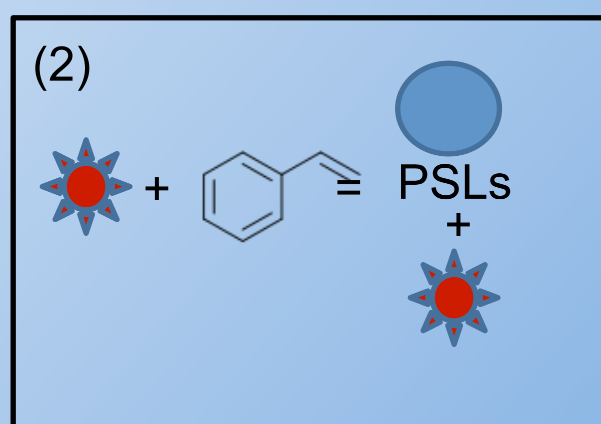
- KR 620 was average but it had been difficult to achieve good <u>incorporation</u> of Kiton Red 620 into the PSLs and difficult to prevent <u>leaching</u> out afterward.

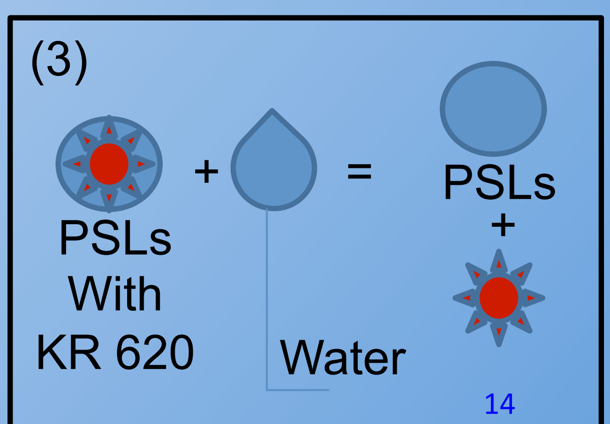
Problems with KR620 doped PSLs

- Previous attempts to incorporate Kiton Red, a non-hazardous chromophore with more desirable spectral properties were hindered due to kiton red 620's:
  - (1) Interference with PSL synthesis
  - (2) Difficulty to incorporate into PSLs
  - (3) Difficulty with leaching out of the PSLs

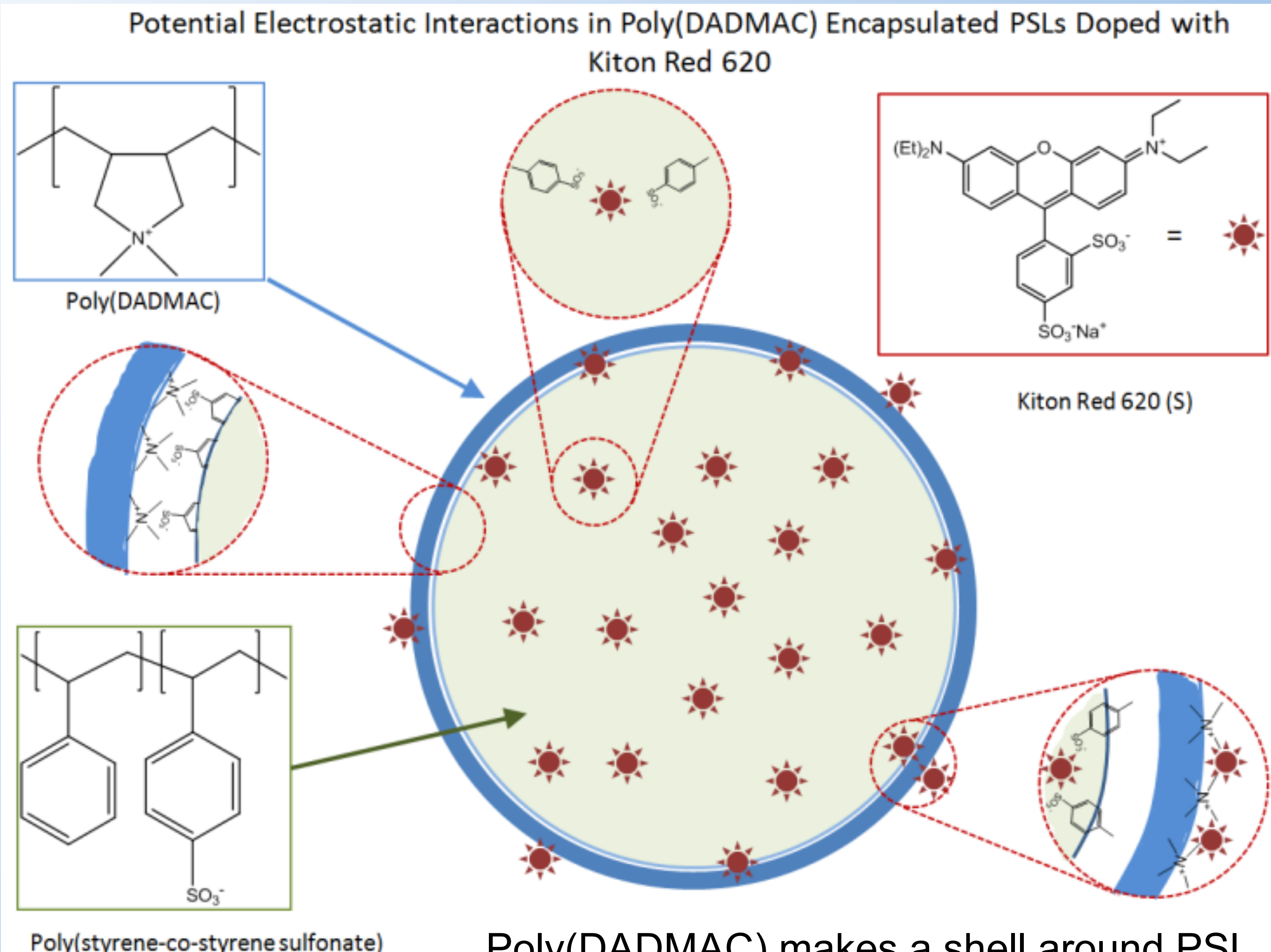








Use of Poly(DADMAC) to prevent leaching and $NaHCO_3$ to prevent coagulation (also helps leaching)



Poly(DADMAC) makes a shell around PSL

Improving KR620 doping

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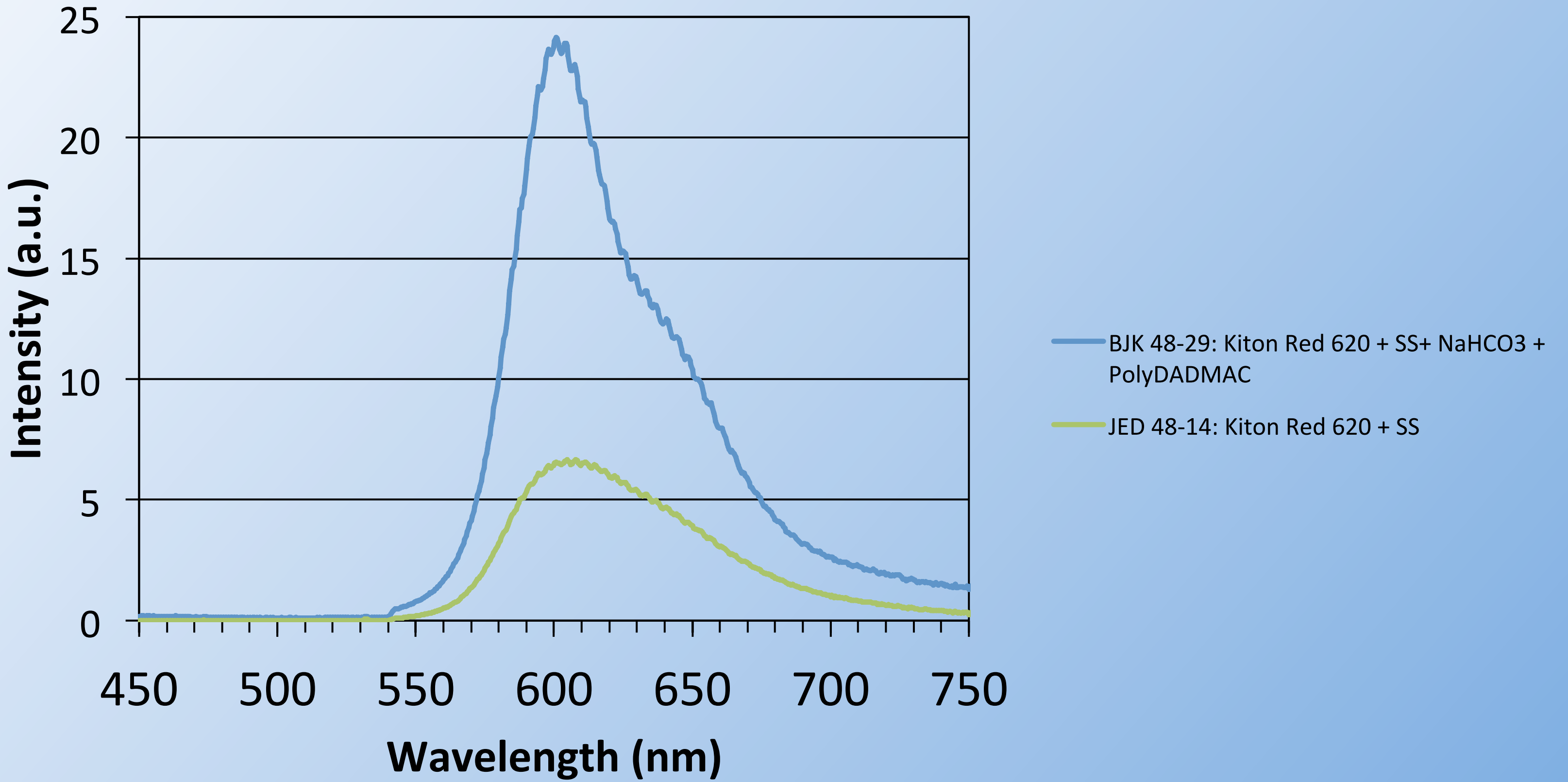
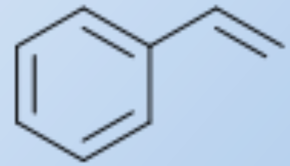


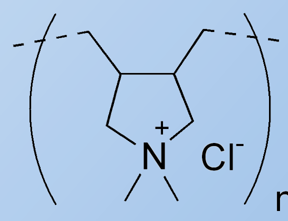
- Using $NaHCO_3$ and PolyDADMAC gave larger signal *and* reduced leaching.
- But was this the optimum formula?

Soap-Free Emulsion Polymerization: Variables

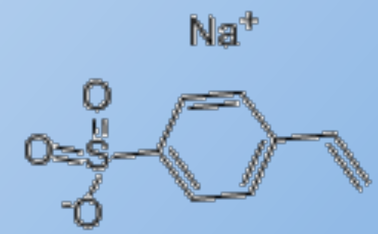
- Process involves many variables
  - Styrene Monomer
  - Styrene Sulfonate
  - Kiton Red 620
  - polyDADMAC
  - $NaHCO_3$ (Sodium Bicarbonate)
  - Potassium Persulfate
  - Temperature
  - Stir Rate



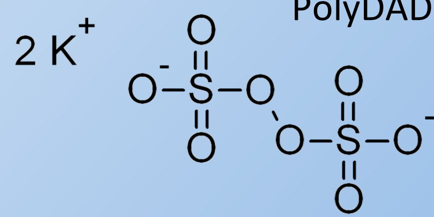
Styrene



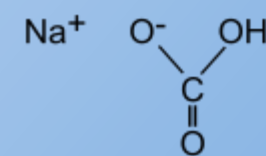
PolyDADMAC



Styrene Sulfonate

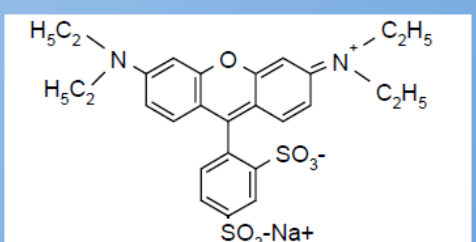


Potassium Persulfate



Sodium Bicarbonate

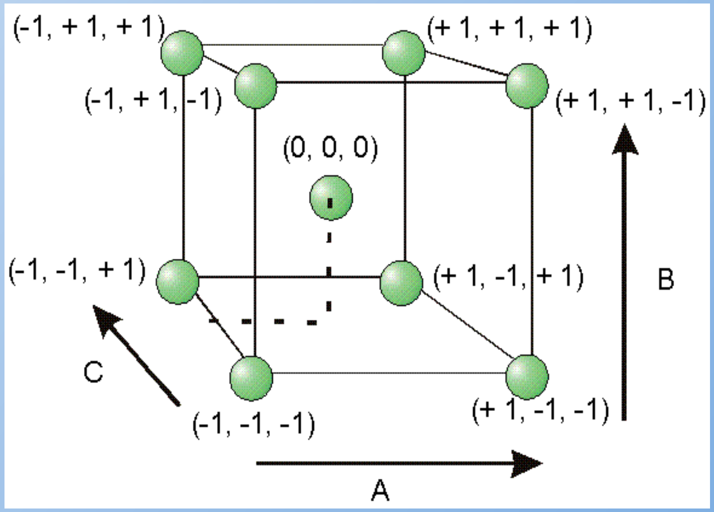
- Design of Experiments: study the effects of <u>four</u> factors:
  - (2^8 = 256; 2^4 = 16)
  - Kiton Red 620 concentration
  - Mole Ratio of Styrene Sulfonate to Styrene Monomer
  - PolyDADMAC
  - $NaHCO_3$



Kiton Red 620

Design of Experiments (DOE)

- Identify significant inputs, *interactions* between inputs, and their effect on the outputs
- Maximum information from minimum number of experiments
  - “Experiments” take 24 hours each
  - Had time to do ~30 experiments
- Basic components of DOE
  - Factors – inputs to process
  - Levels – setting of each factor studied
  - Response – output of experiment
- Chose a 4-factor, 2-level Full Factorial Design with 8 center points
  - 24 experiments in total ($2^4 + 8$)



Example of design space for 3 factor, 2 level, full factorial with center point

DOE Test Matrix

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Standard Order	Run Order	Block	Kiton Red 620 (mg)	Styrene Sulfonate / Styrene Ratio	PolyDADMAC (g)	$NaHCO_3$ (g)
1	14	2	5	0	0	0
2	1	1	50	0	0	0
3	8	1	5	6/94	0	0
4	23	2	[illegible]	[illegible]	0	0
5	5	1	[illegible]	[illegible]	1	0
6	20	2	[illegible]	[illegible]	1	0
7	21	2	[illegible]	[illegible]	1	0
8	4	1	[illegible]	[illegible]	1	0
9	10	1	[illegible]	[illegible]	0	1.5
10	18	2	[illegible]	[illegible]	0	1.5
11	17	2	[illegible]	[illegible]	0	1.5
12	12	1	[illegible]	[illegible]	0	1.5
13	22	2	[illegible]	[illegible]	1	1.5
14	2	1	[illegible]	[illegible]	1	1.5
15	7	1	[illegible]	[illegible]	1	1.5
16	16	2	[illegible]	[illegible]	1	1.5
17	9	1	[illegible]	[illegible]	0.5	0.75
18	3	1	[illegible]	[illegible]	0.5	0.75
19	6	1	[illegible]	[illegible]	0.5	0.75
20	11	1	[illegible]	[illegible]	0.5	0.75
21	13	2	27.5	3/94	0.5	0.75
22	24	2	27.5	3/94	0.5	0.75
23	15	2	27.5	3/94	0.5	0.75
24	19	2	27.5	3/94	0.5	0.75

Made 32 total batches

DOE: Results

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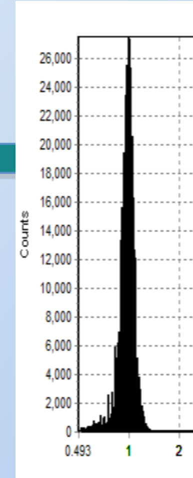
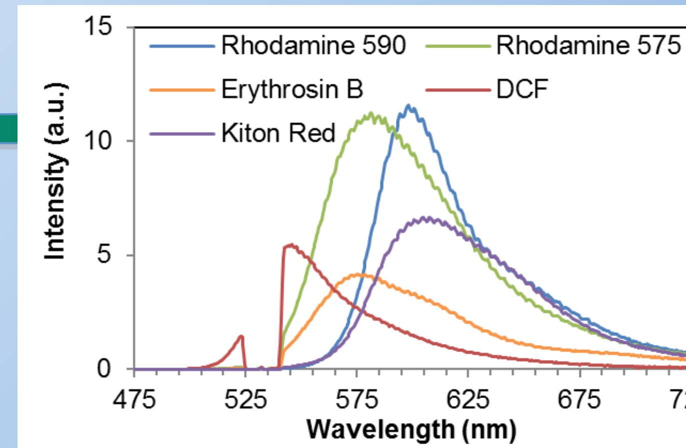
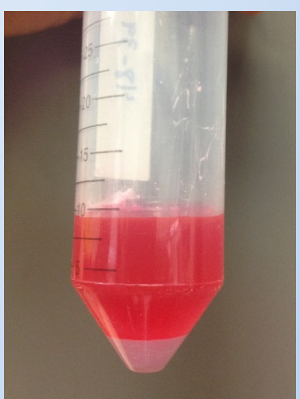
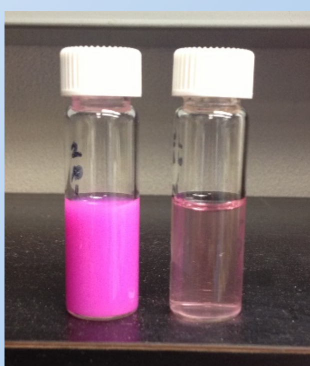


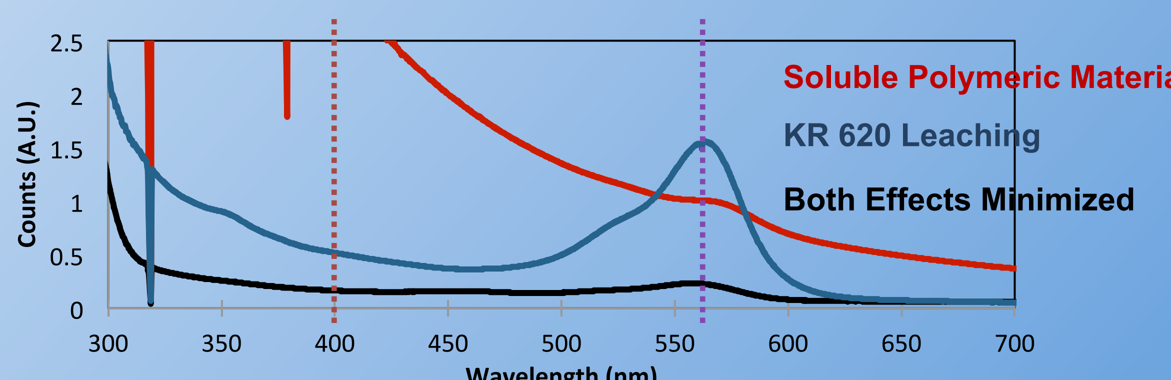


Responses (Dependent Variables):

- <u>Particle Size Data</u>-
  - Particle diameter mean and mode
  - Particle size distribution (σ)
- <u>Fluorescent Emission Intensity</u>-comparison of potential LIF signal strength
- <u>Leaching Spectral Data</u>-absorption characteristics of supernatant once PSLs were removed via centrifugation
  - Absorption at **400 nm**-indicative of soluble polymeric materials
  - Absorption at **565 nm**-indicative of KR 620 leaching from PSLs







Outcome of DOE Study

- A recipe that optimized the outputs was developed using small (0.25 L) batches
- Data was studied to gain insight into which parameters affect different outputs (ongoing)
  - For example, 3 of the inputs affected leaching
- Small (0.25 L) batches closest to optimized result were sent to Virginia Tech for further testing
- Large (4L) batches were made using optimized recipe.

Large Scale Kiton Red PSL Synthesis

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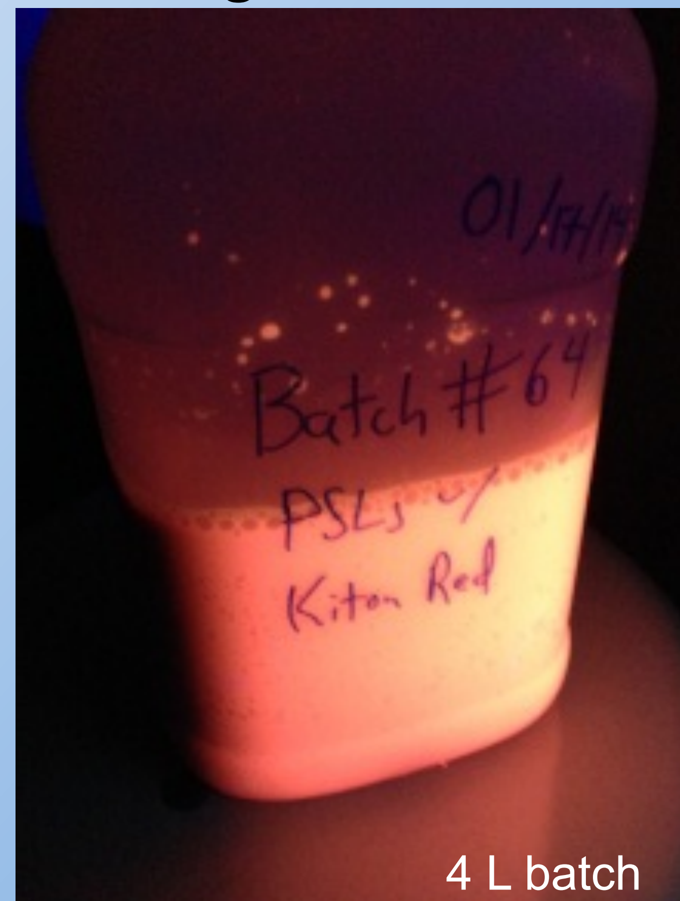
Pictures of KR620 PSL Production

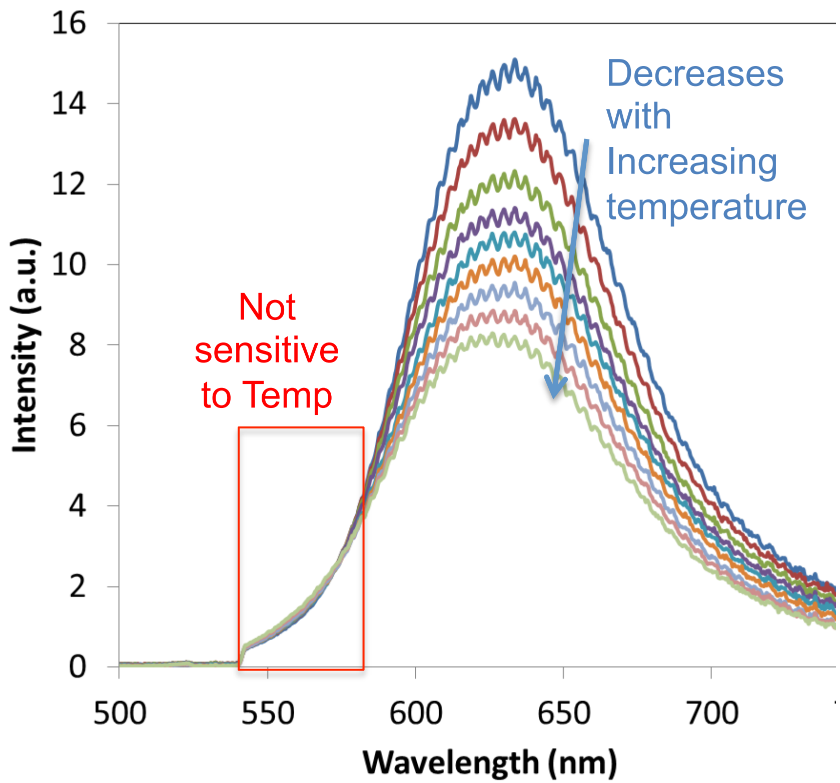
Before Polymerization

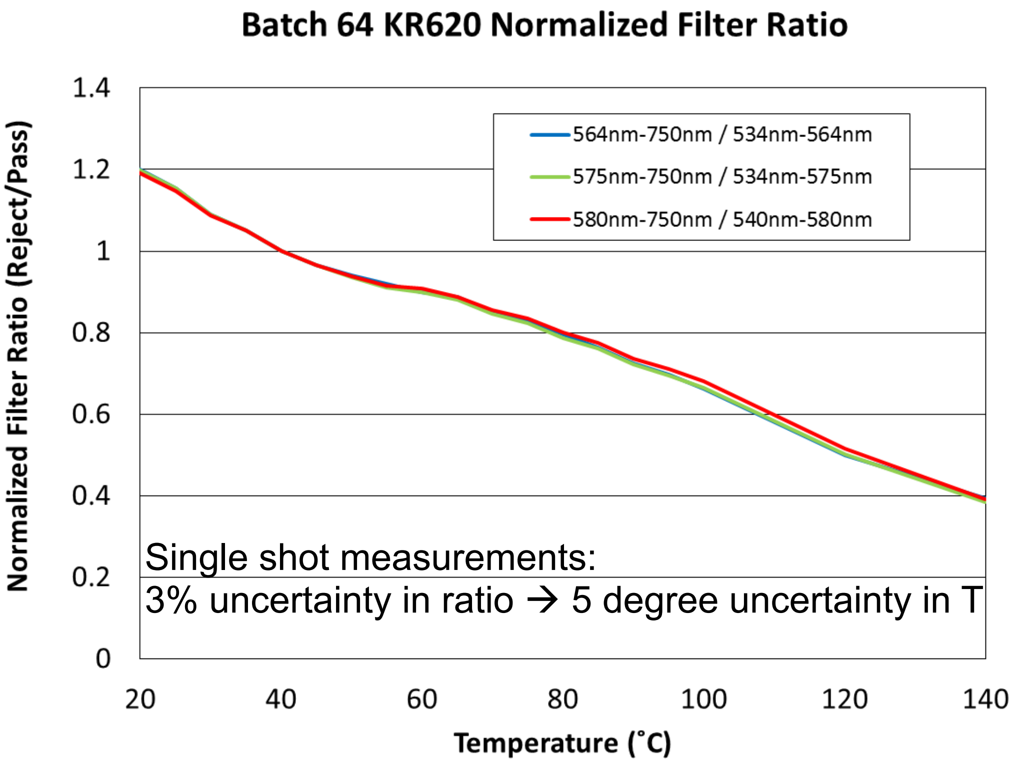
After

Resulting batch of Particles



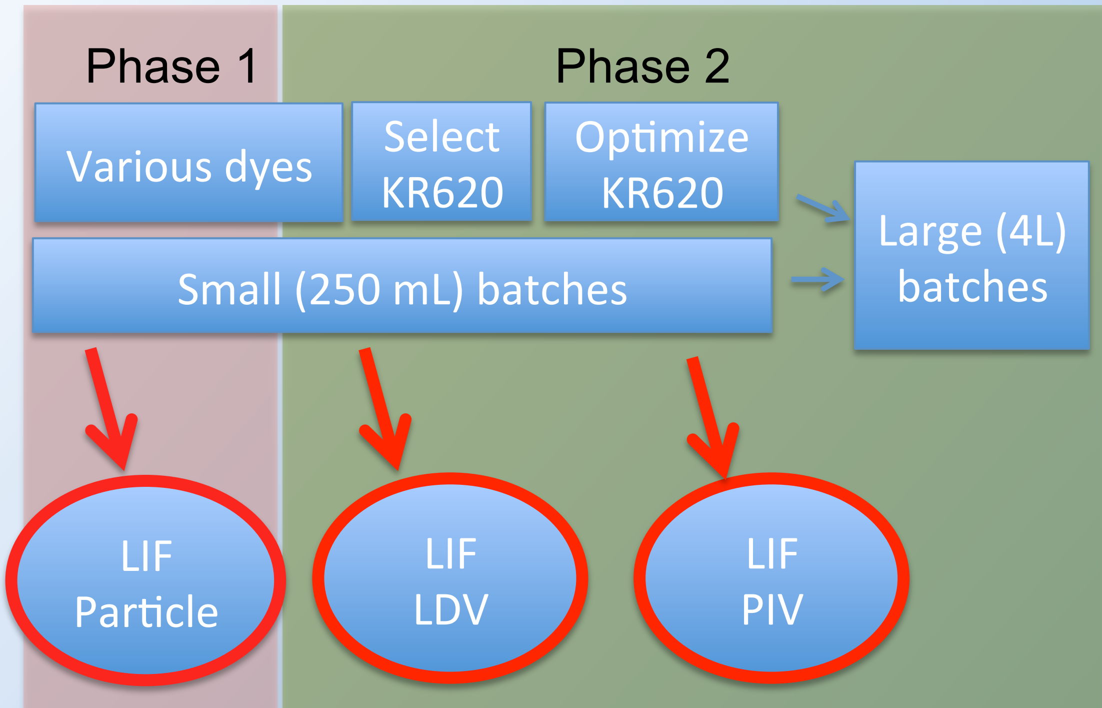
Characterization of Large KR620 Batch 64





- Measured spectra versus temperature (dry particles on hot plate)
- Look at *ratio* of LIF spectral bands = f(Temperature)
  - Ratio varies a factor of 3 from 20 C to 140 C
  - Measure ratio: relate to unique temperature

Graph of Project Progress



Work done at Virginia Tech

iphone camera looking through laser goggles

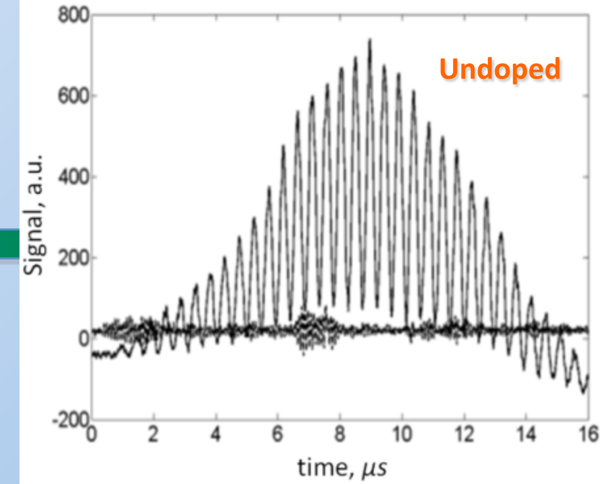
Fluorescence-based LDV

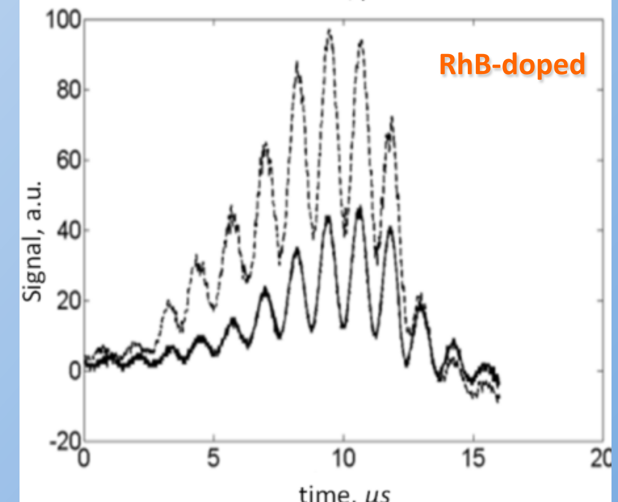
- **Laser Doppler Velocimetry (LDV) via the fluorescence signal from dye-doped PSLs.**
  - **Work performed at Virginia Tech, Blacksburg, VA**

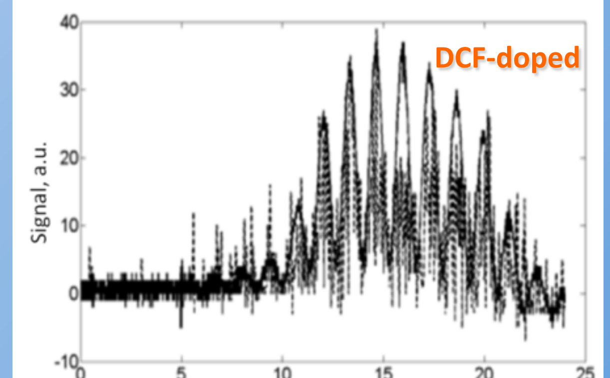
- **Quality of LDV signal obtained via SNR measurements.**
  - **RhB-doped particles produced ~95% validation of LIF velocimetry signal.**
  - **Results worse with DCF, but still usable.**
  - **Resulted in Journal publication:**

    K. T. Lowe, P. Maisto, G. Byun, R. L. Simpson, M. Verkamp, P. M. Danehy, P. I. Tiemsin, and C. J. Wohl "Laser velocimetry with fluorescent dye-doped polystyrene microspheres," Optics Letters Vol. 38, No. 8 p. 1197-1199, April 15, 2013.

- **New KR620 signals are similar to Rhodamine B**
  - **Not tested, but expect similar results as Rh B with KR620**



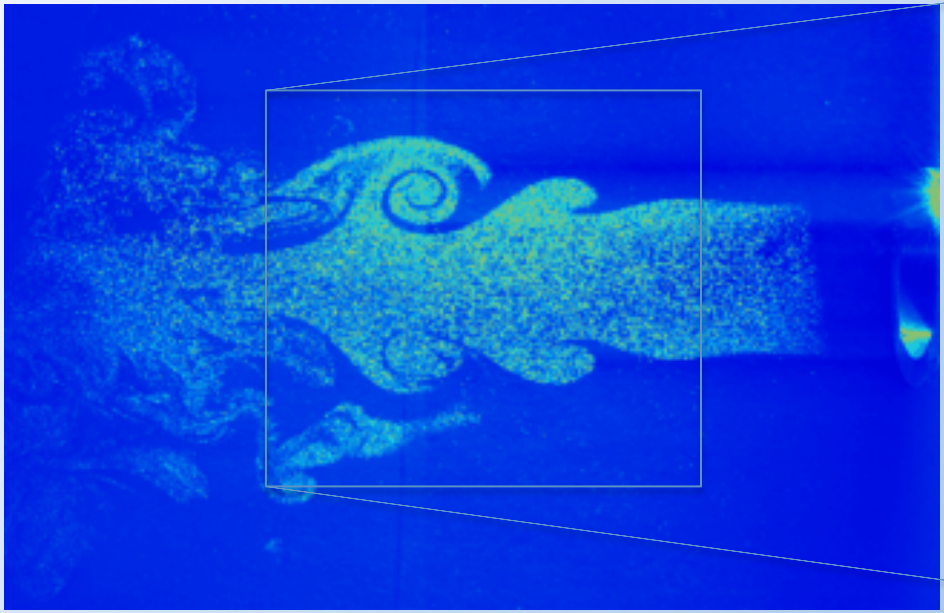




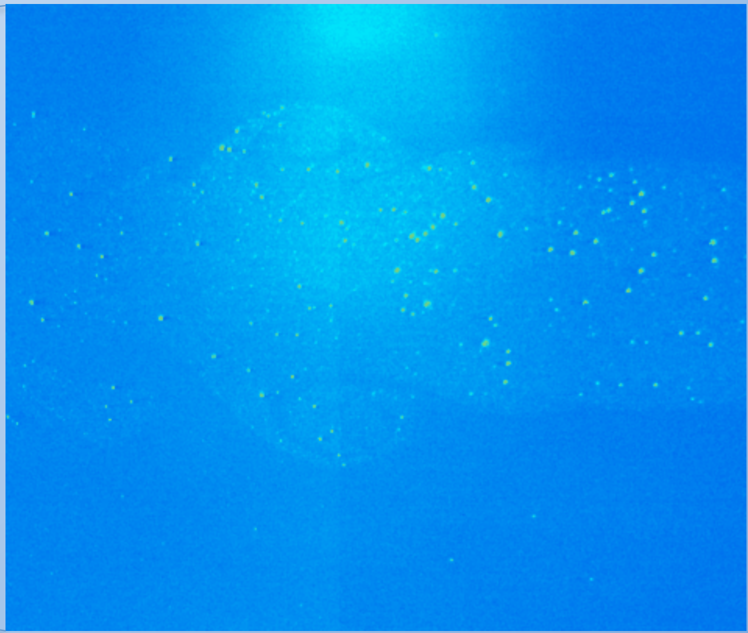
Single-particle bursts from Mie (solid) and LIF (dashed) signals.

Single-laser-pulse imaging

Mie scattering



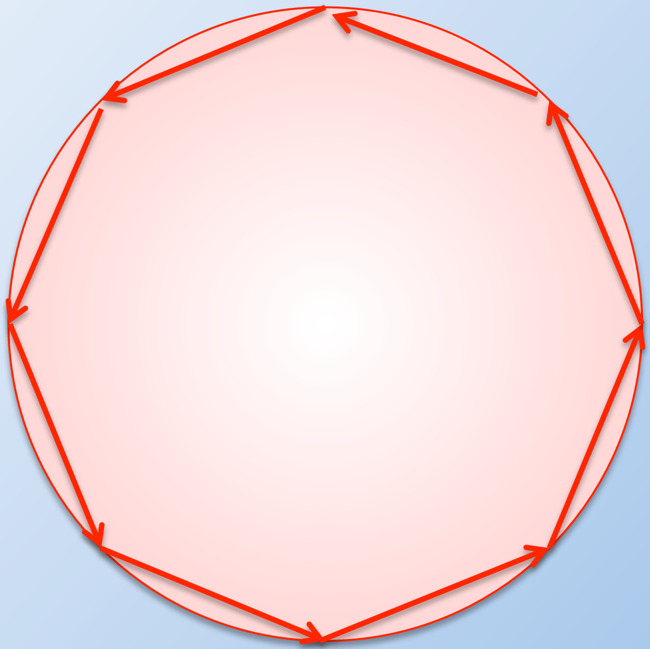
LIF:

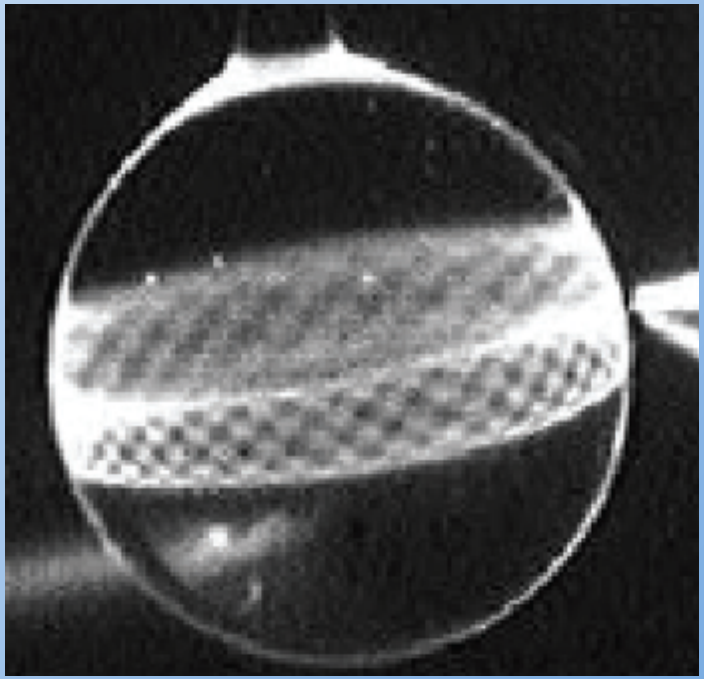


- Jet seeded with dye-doped particles (KR620, small batch)
- 10 Hz single-pulse laser, 200 mJ/pulse, 532 nm
- Mie scattering (F/22, no filter) shows expected uniform distribution of particles
- LIF imaging (F/2.8, 580 nm long-pass filter) shows fluorescence but bimodal distribution in intensities (some bright, some dim) [LIF is 100x lower than Mie]
- No evidence of agglomeration in Mie scattering signal

Are Bright particles actually lasing? Whispering Gallery Modes

- Phenomena discovered at St Paul's Cathedral explained by Lord Rayleigh (1878)





For dye-doped particles excited by a laser, can exhibit gain: very bright LIF
Light output frequency is f(diameter)
Studied by T. Ioppolo (SMU) and others.

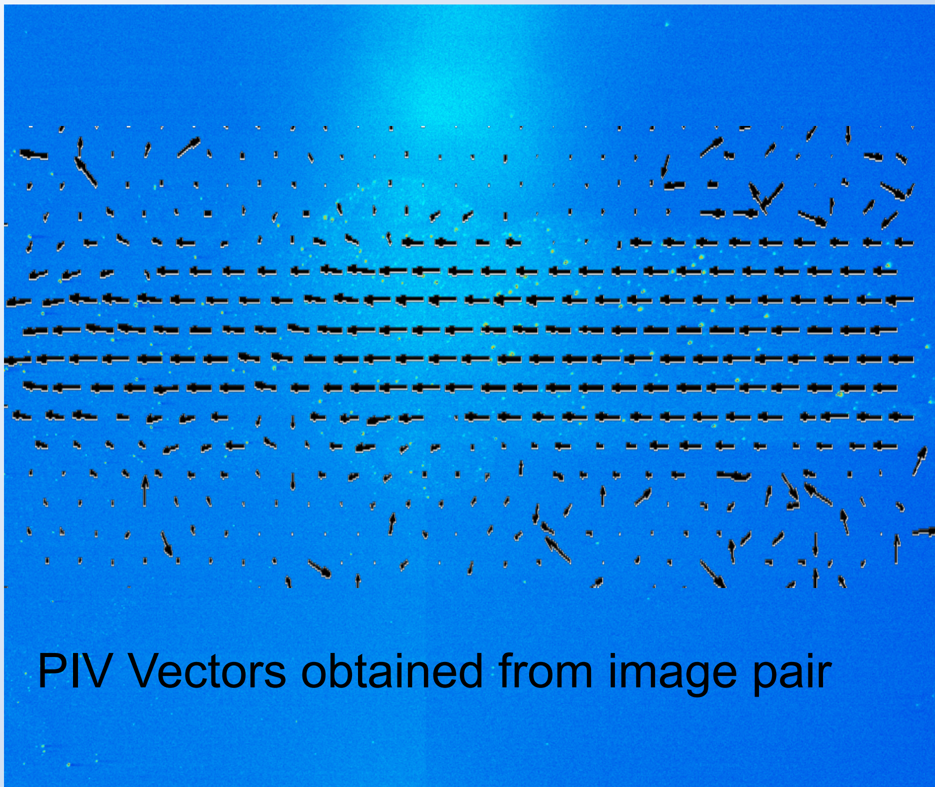
Caltech/NASA Tech Briefs
http://www.techbriefs.com/component/content/article/3160

Need to understand this, control it.
Measure pressure? Temperature?

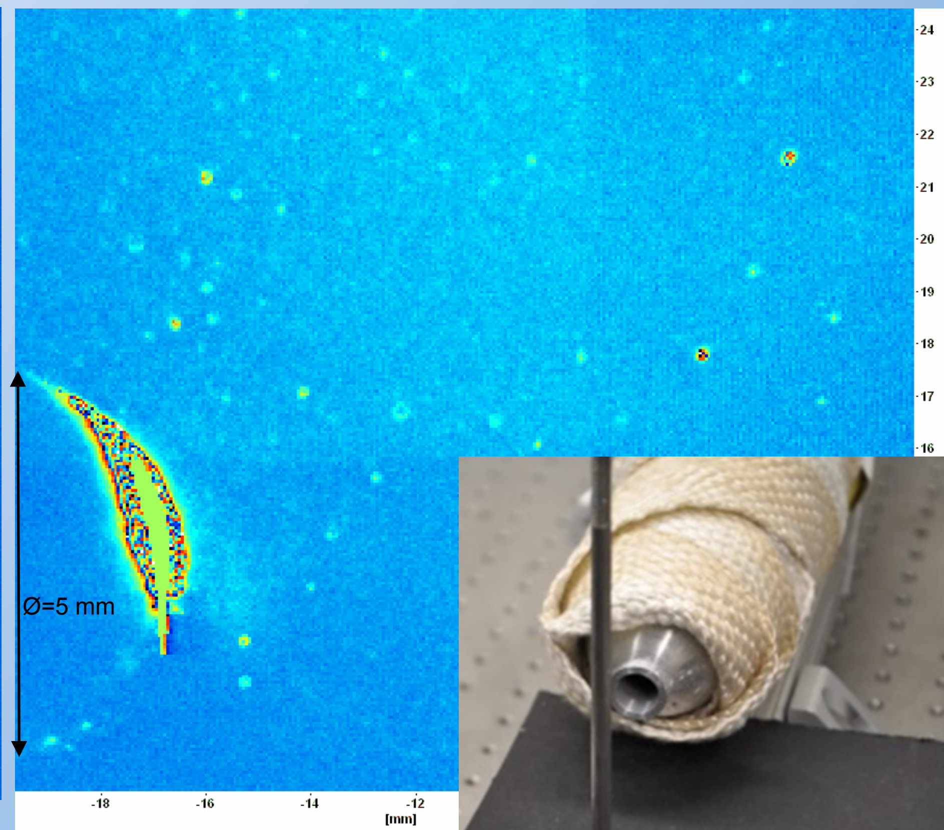
Kiton Red 620 PIV (Double Pulsed Excitation)

- Double-pulsed fluorescence signal from Kiton red doped particles in a jet: Fluoresence-based PIV

- Zoomed view of particles near an obstacle. Illustrates clearly the wide range of emission intensities.



PLIF Double Pulse Frame from a probe area of the free jet illuminated with 200 mJ/pulse.



PLIF Double Pulse Frame in the proximity of a Rod using 200 mJ/pulse.

Innovation: Key Points

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- Identified multiple (and demonstrated some) measurement approaches with different dyes and different laser and detector configurations to measure:
  - Temperature, Pressure, Concentration
  - Pointwise (fast) or imaging (10 Hz) are possible
  - Alone or simultaneous with LDV, PIV
- PSLs have been synthesized with a variety of different dyes – different colors
  - Dye influence on particle size and size distribution was observed and characterized
  - Different methods of incorporating dyes explored
  - KR620 doping process was optimized
  - Large batches of KR620 were produced, providing ucing enough material for extensive measurements in large scale facility
- Laser-induced fluorescence LDV, PIV and (preliminary) temperature measurement in jet flows using a safe dye were demonstrated with partner (VT, POC: Todd Lowe) for the first time.
- Clear path forward for simultaneous temperature-velocity measurements with PIV, LDV that are expected to be completed before end of project funding.

Impact of Innovation if Incorporated

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- **Extend measurement technology beyond force/moment/wall and u, v velocity measurements**
  - Temperature, Pressure, Concentration
- Impact on NASA ARMD Programs:
  - SFW/ERA: Jet noise studies, T, u, v and correlations
  - Rotary Wing: Pressure disturbances near blade tips
  - High Speed: Sonic Boom simultaneous P, u, v measurement
  - Measurements would provide unique data for validating CFD codes in a way not currently possible.
- Have identified potential customers within NASA, at other government agencies, academia and industry.
  - George Washington Univ., NASA Langley, NASA Ames, etc.

Conclusions

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- Developed new generation of particle-based instrumentation for wind tunnels
  - Potential shown to measure Temperature, Concentration
  - Can use much of same equipment as LDV and PIV
- Have successfully doped safe KR620 dye into particles
  - Safer than carcinogenic Rh B used previously
  - DOE study optimized recipe for particles
    - High signal/noise, low leaching, good particle size
  - Small and large batches manufactured
  - Particles show measurable temperature sensitivity
    - Should be able to achieve single shot temperatures
- Demonstrated LDV and PIV using fluorescent PSLs

Graph of Project Progress

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Phase 1

Phase 2

Various dyes

Select KR620

Optimize KR620

Small (250 mL) batches

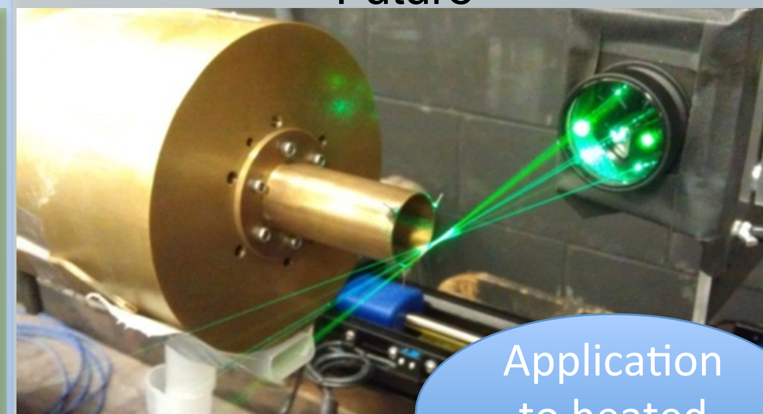
Large (4L) batches

LIF Particle

LIF LDV

LIF PIV

Future



LIF PIV and LDV thermometry

Application to heated jet at VT

Applications at NASA

Unexpected outcomes: New opportunities?

- Expect continuing work with dye-doped PSLs

Next Steps

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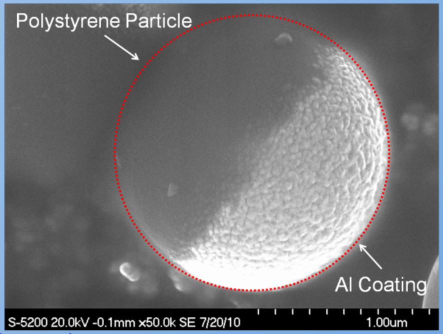
- Continue to analyze results of DOE
  - Journal Article in preparation
- Demonstrate LDV and/or PIV + temp. measurement
  - Virginia Tech funded through end of July to perform demonstrations
  - Only received large batches of KR620 in late January
  - Inorganic seed materials: higher temperature operation
  - Apply to transonic, heated, free jet at VT
- Other fluid dynamics applications at NASA
- Other measurement opportunities:
  - WGM pressure measurement?
  - Asymmetric coated PSLs?



Distribution/Dissemination

Journal:

- K. T. Lowe, P. Maisto, G. Byun, R. L. Simpson, M. Verkamp, P. M. Danehy, P. I. Tiemsin, and C. J. Wohl "Laser velocimetry with fluorescent dye-doped polystyrene microspheres," Optics Letters Vol. 38, No. 8 p. 1197-1199, April 15, 2013.
- Kiefer, Jacob M.; Tiemsin, Pacita I.; Danehy, Paul M.; Lowe, K. Todd; Maesto, Pietro M.F.; Wohl, Christopher J. "Synthesis of Fluorophore-doped Polystyrene Microspheres: Optimization through Design of Experiments Methodologies" Macromolecules, 2014, manuscript in preparation.

Conference:

- Verkamp, Max A.; Danley, Jason, E.; Maesto, Pietro M.F.; Koh, Brian; Lowe, K. Todd; Tiemsin, Pacita I.; Danehy, Paul M.; Wohl, Christopher J. "Fluorescent Dye-Doped Polystyrene Microspheres for Particle Image Velocimetry" 246th American Chemical Society National Meeting, Indianapolis, IN, September 8-12, 2013.
- P.M.F. Maisto, K. T. Lowe, G. Byun, R. Simpson, M. Verkamp, J. Danley, B. Koh, P. I. Tiemsin, P. M. Danehy, C. J. Wohl, "Characterization of fluorescent polystyrene microspheres for advanced flow diagnostics" AIAA Fluids Meeting, San Diego, June, 24-27 2013.

Patent:

- Danley, Jason E.; Tiemsin, Pacita I.; Wohl, Christopher J. Dye-doped Polymer Microparticles, LAR-18344, 2013, provisional patent application filed.

Thesis:

- P.M.F. Maisto, "Experimental analysis and prospective flow diagnostic applications for fluorescence dye-doped micro-particles," M.S. Thesis, Virginia Polytechnic Institute and State University, submitted 21 February 2014.

NASA Technical Memorandum:

- P. M. Danehy, P. Tiemsin, C. Wohl, M. Verkamp, T. Lowe, P. Maisto, G. Byun, R. Simpson, "Fluorescence-Doped Particles for Simultaneous Temperature and Velocity Imaging," NASA Technical Memorandum, NASA/TM-2012-217768, September, 2012.

Backup Charts

End of Phase 1 Results

- Doped several different dyes into PSLs with varying degrees of success
  - Low signals, leaching problems, etc.
  - Rhodamine B (toxic) still had the largest fluorescent signal
- Demonstrated LIF from particles in a setup similar to, but not LDV
- Demonstrated a temperature measurement by ratio of LIF to Mie scattering but very imprecise due to particle size variation

Spectral Characterization Set Up

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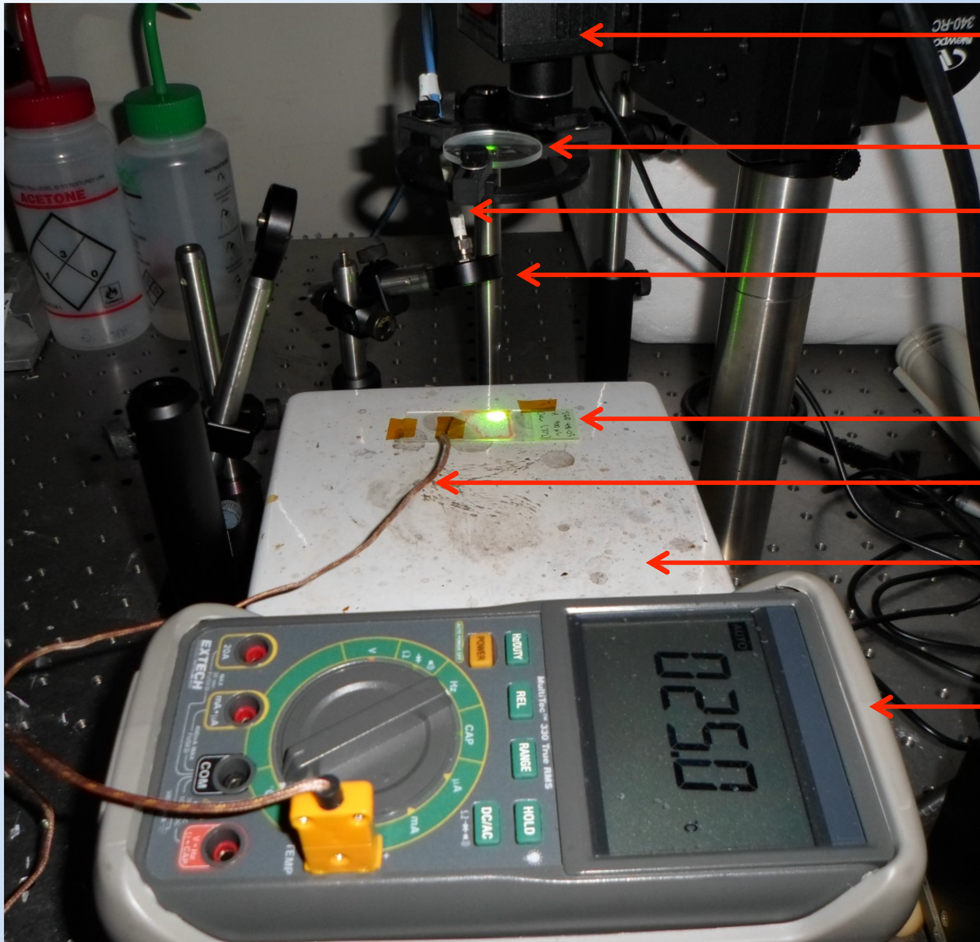

Nd:YAG Laser (532 nm)

Concave Lens

Fiber Optics (to Spectrometer)

Semrock (532nm)Blocking Filter

Slide Sample

Thermocouple

Hot Plate

Multimeter

Fluorescent particle past work

- **Literature Review:**
- Found no past work using doped PSL for thermometry
- Kimura et al. (2006) used PSLs painted with PSP to measure pressure.
- Fluorescein 27 is very attractive for temperature sensitivity, on the order of 3.5%/°C (Dunand et al. 2010 and Sutton et al. 2008)
- Multiple dye techniques may offer significant advantages for improved sensitivity (Sutton et al. 2008).
- US Patent 4194877 claims invention of dye-doped PSLs.

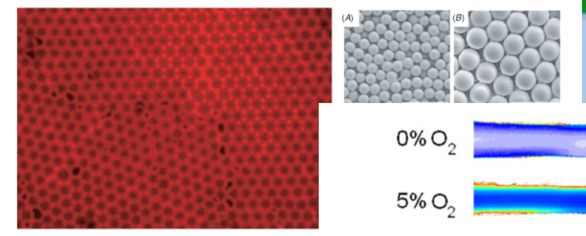

Figure 4. Left: phosphorescence microscopy images of PSBeads 3.0 μm in SiOEP and PtOEP that were synthesized with different AIBN concentration

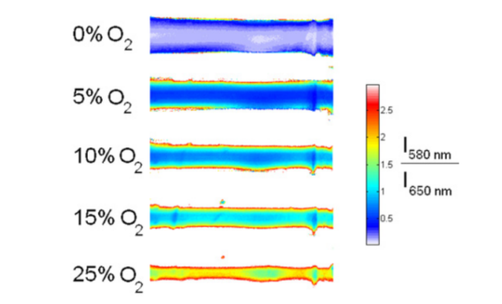

Figure 8. PSBeads ratio of $I_{580\ nm}/I_{650\ nm}$ images excited by a 400 nm laser in 0%, 5%, 10%, 15%, 25% and 30% oxygen concentrations.

Pressure sensitive PSLs and results of Kimura et al. (2006).

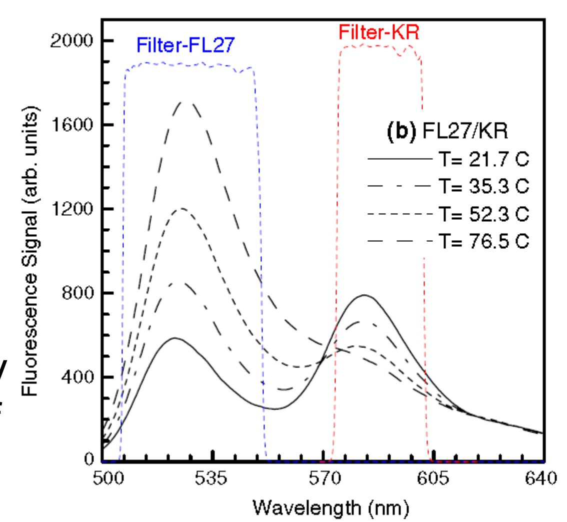

Fig. 12 Relative emission spectra of FL27/RhB mixtures (**a**) and FL27/KR mixtures (**b**) in water for temperatures ranging from 22 to 78°C. Also shown are the "filter masks" used for evaluating the ratiometric technique

Two-dye thermometry technique of Sutton et al. (2008).

Fluorescent particle past work

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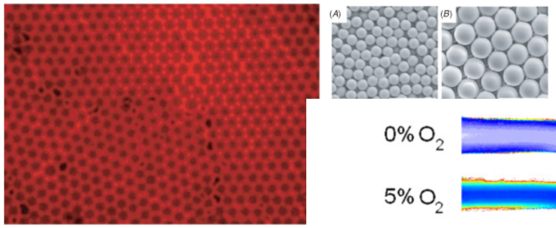
- To our knowledge no past work has leveraged doped PSLs for particle temperature measurement in flows.
  - Kimura et al. (2006) used PSLs painted with PSP to measure pressure.
- For particles in a flow, only Kimura et al. (2006) and the group from Georgia Tech and Metrolaser (Jain et al. 2011) have attempted measurements of particles on the order of 1um; i.e., in the size range needed for time-resolved measurements
- To our knowledge, no one is addressing static temperatures colder than ambient, as done here.
- According to Dunand et al. (2010) and Sutton et al. (2008), Fluorescein 27 is very attractive for temperature sensitivity. The authors report sensitivity on the order of 3.5%/^{o}C.
- Multiple dye techniques may offer significant advantages for improved sensitivity (Sutton et al. 2008).
- Transmission within particles has been studied with implications to current work in which directivity of the fluorescence emission may be leveraged (Kuwata-Gonokami et al. 1992 and Frackowiak and Tropea 2010).
- US Patent 4194877 claims invention of dye-doped PSLs.



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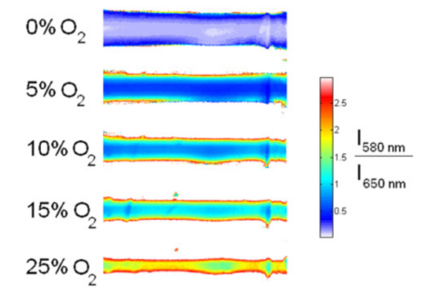

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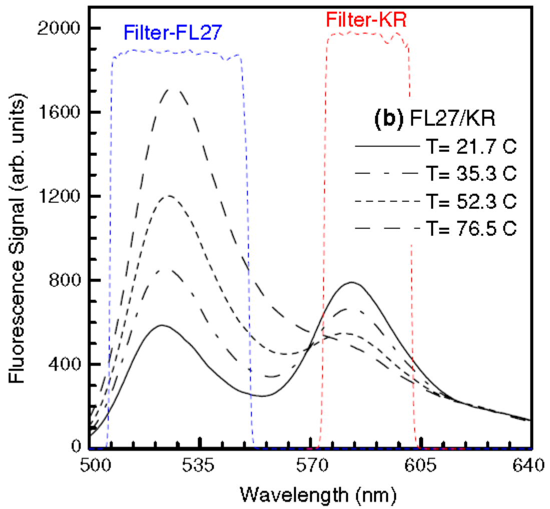

Fig. 12 Relative emission spectra of FL27/RhB mixtures (**a**) and FL27/KR mixtures (**b**) in water for temperatures ranging from 22 to 78°C. Also shown are the "filter masks" used for evaluating the ratiometric technique

Phase I Results: Concept Demo II

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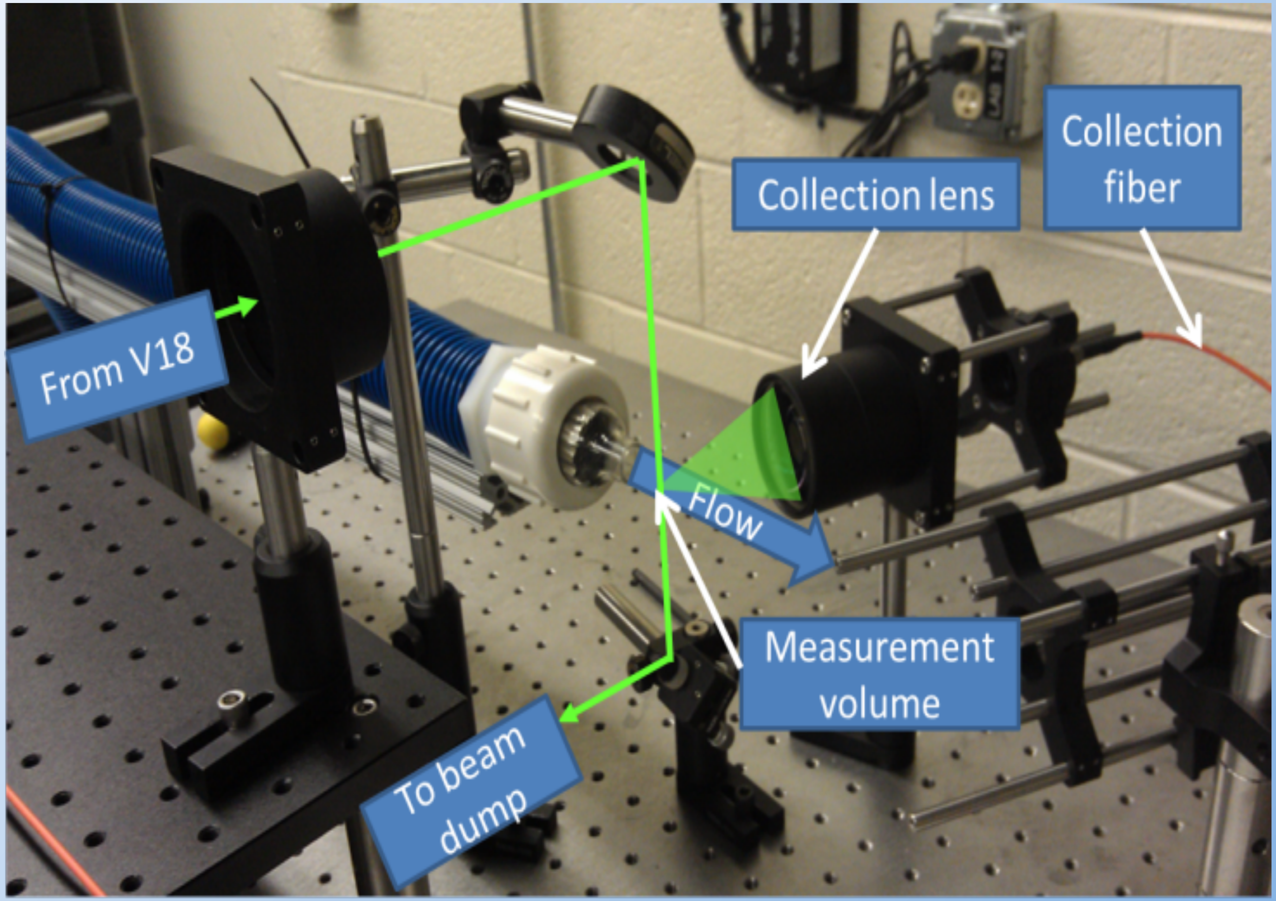
5 W laser



PMT detection

(Lowe, VT)

- Split collected light into two channels: Mie (532 nm) & LIF (>600 nm)
- Added dry ice to flow to vary temperature; monitor with thermocouple

Phase I Results: Concept Demo III

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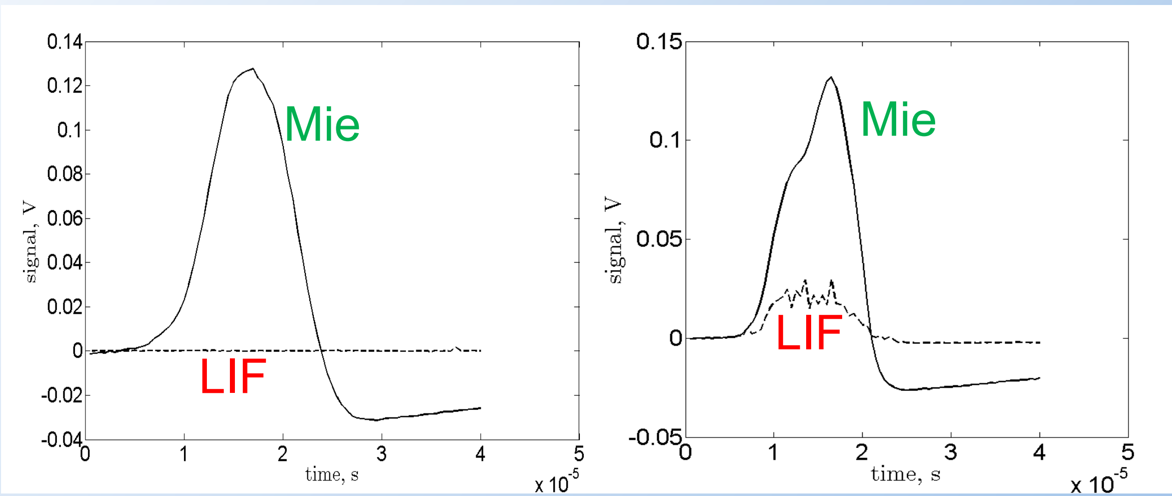
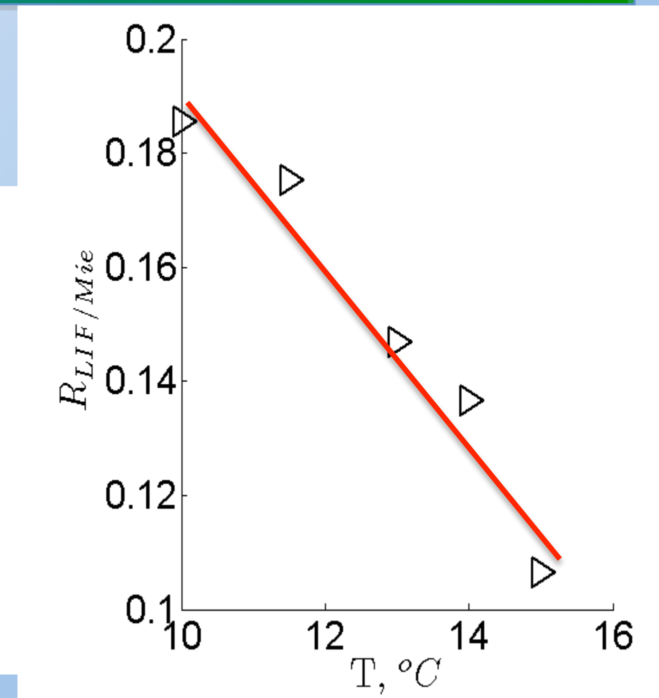
Scattering traces from single particles

No dye in PSL: With dye in PSL:





- Mie scattering provided plenty of signal for velocimetry (though not demonstrated in this experiment).
- LIF channel provided sufficient signal for temperature determination (using Mie as reference)
- Temperature range in proposed experiments will be larger

(Lowe, VT)

Single-shot temperature precision

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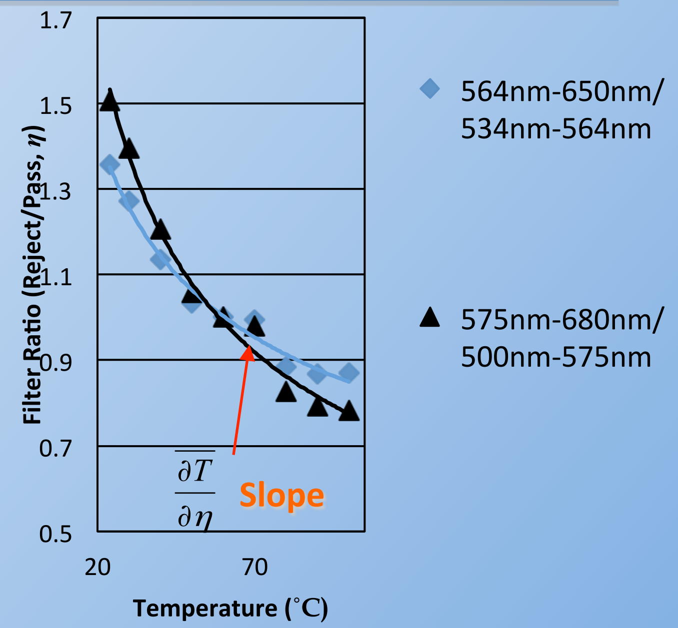
- **Single-shot temperature uncertainties are dominated by**
  - **SNR-limited LIF ratio standard deviation:** $\delta\eta$
  - **And the LIF temperature sensitivity:** $\dfrac{\partial T}{\partial \eta}$
- **Relating,**

$$\delta T \approx \pm \frac{\partial T}{\partial \eta} \delta\eta$$



➢ **<u>Current capabilities provide ±12.5°C</u> precision, while sensitivity or SNR improvements may yield sub-degree resolution.**

0.025	±3.1°C	1.7	0.8	0.4	0.2
0.05	6.3	3.3	1.7	0.8	0.4
0.1	12.5	6.6	3.3	1.5	0.7
0.2	25.0	13.2	6.6	3.0	1.4