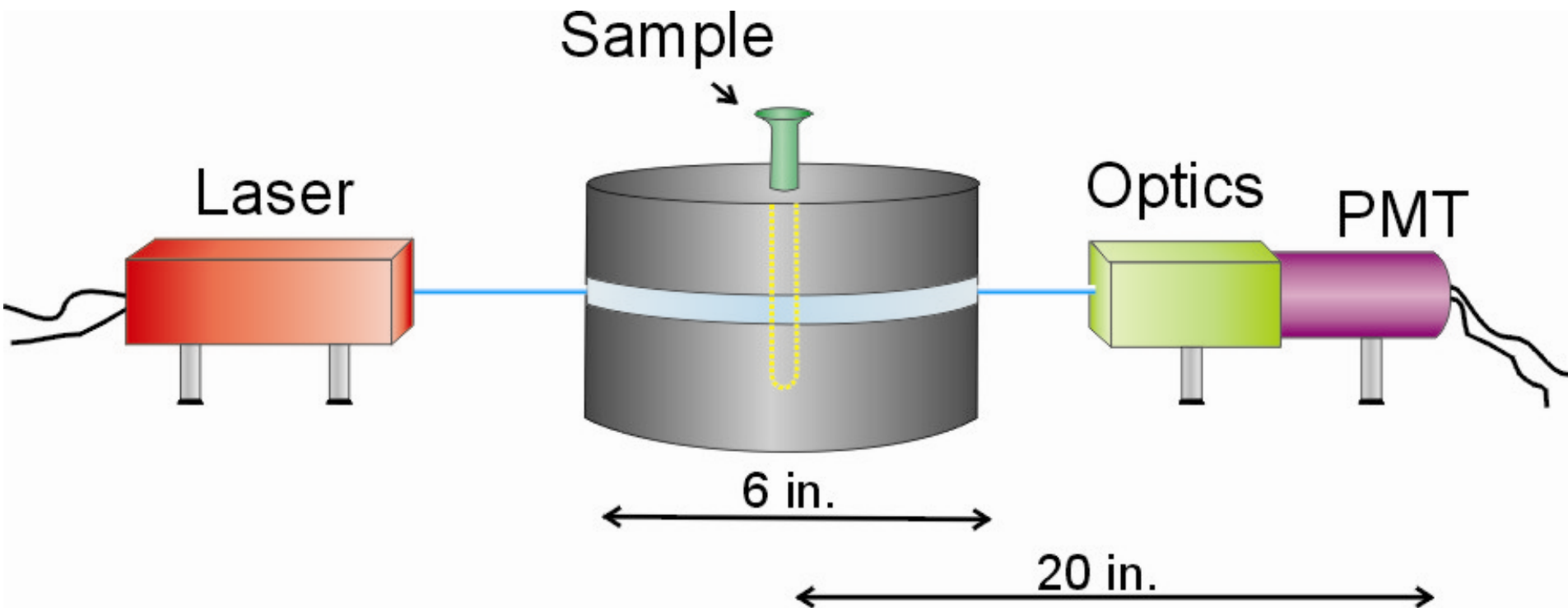


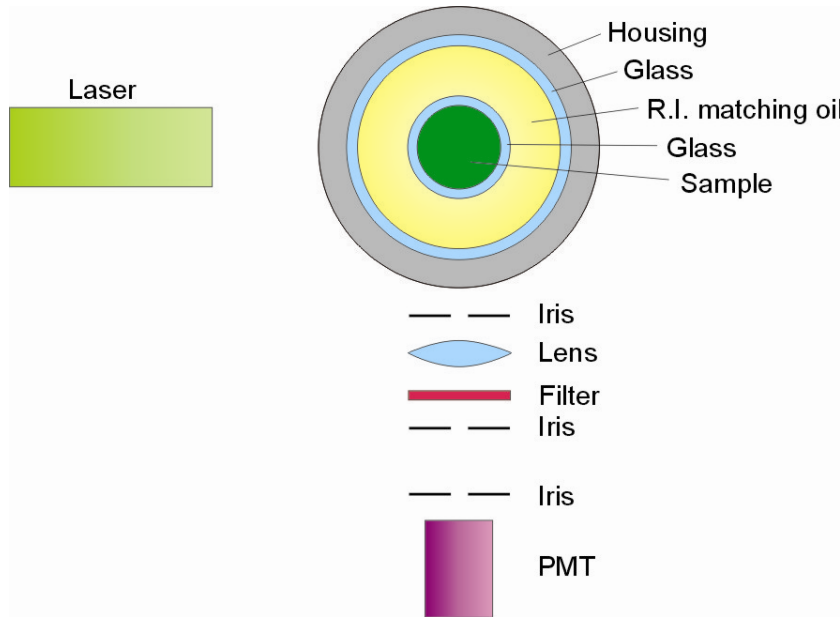
Microfluidic Dynamic Light Scattering

Tom Chastek

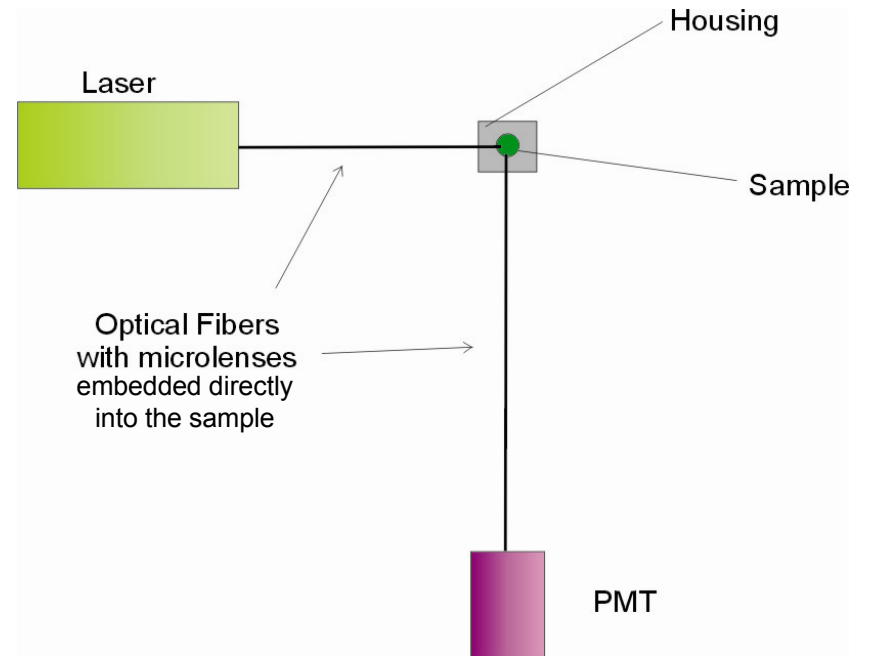
Traditional dynamic light scattering instrument

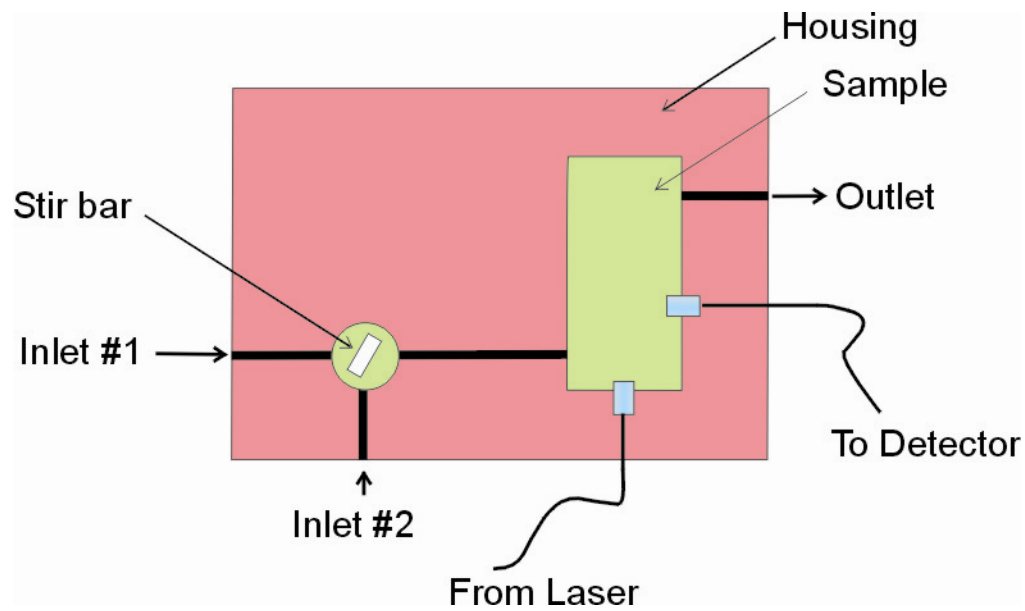


Traditional DLS instrument – TOP VIEW



Microfluidic DLS instrument





Dimensions

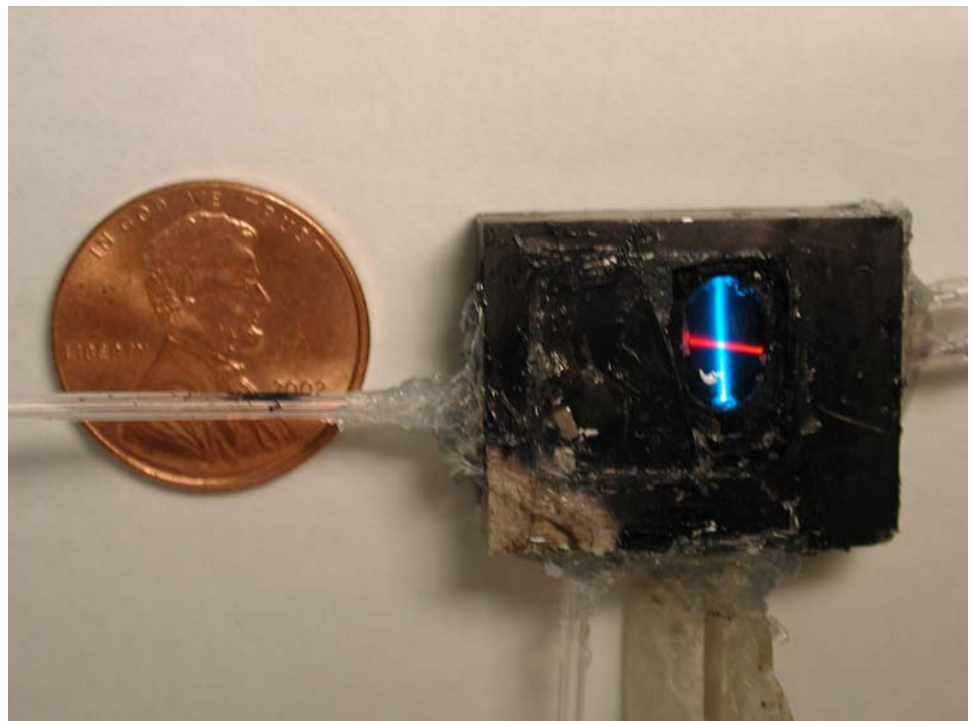
Overall: 20 x 25 x 7 mm

Detecting cavity: 7 x 5 x 2 mm, 70 μL

Mixing cavity: 5 mm diameter x 2 mm = 40 μL

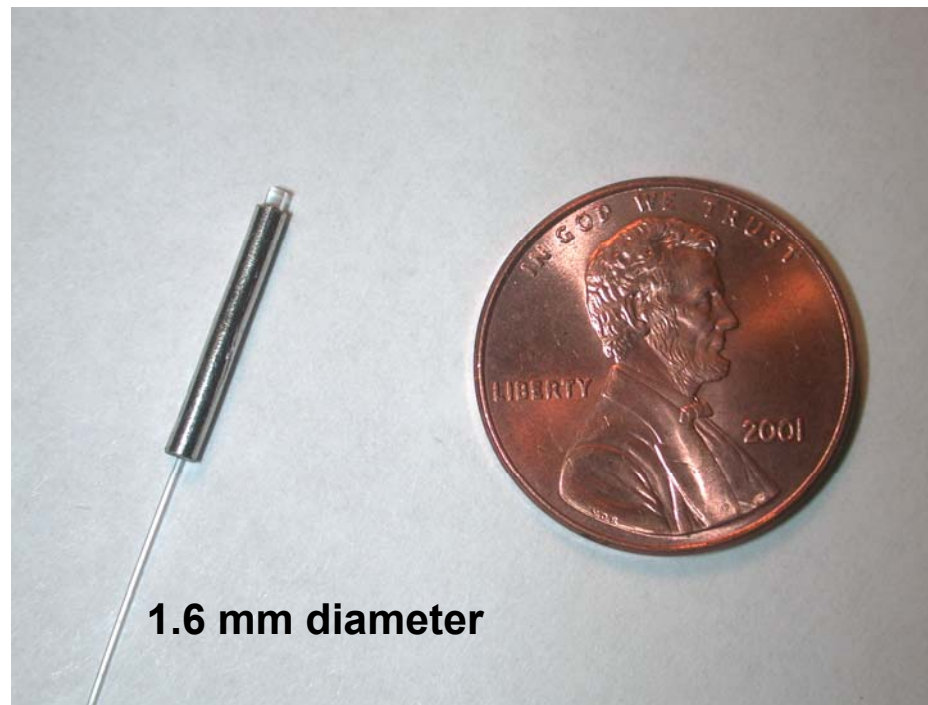
Micro lens: 1 mm diameter, 3.1 mm long

Fiber optic: overall – 254 μm
active area - $\sim 5 \mu\text{m}$

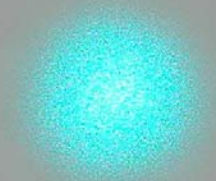


Red laser light sent through detector fiber

Fiber optic probe with microlens



Beam divergence at 3 meters



2.92 mrad



0.91 mrad

Red helium-neon laser used as reference

Beam diameter:

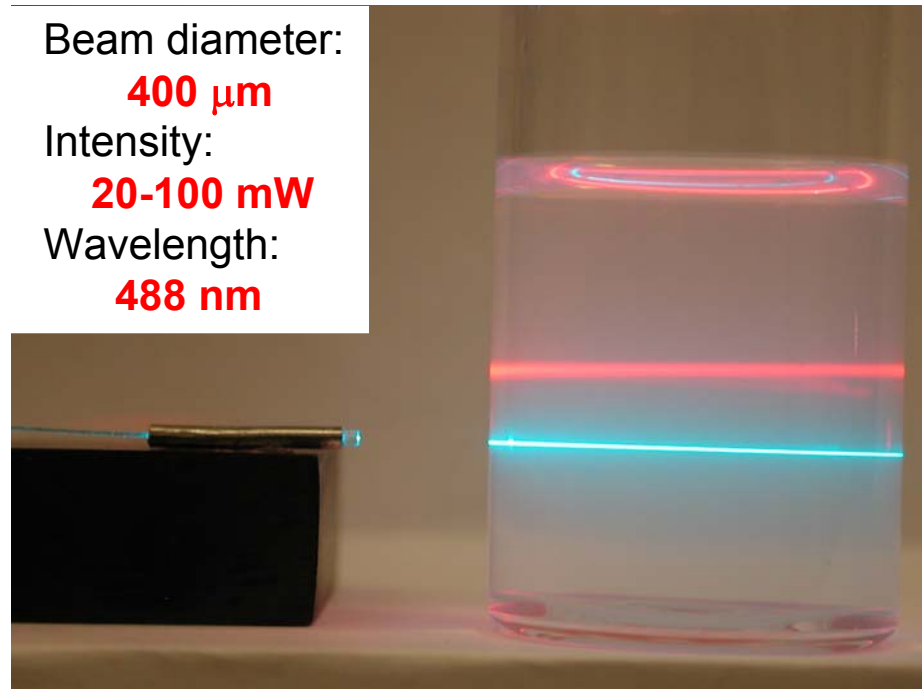
400 μm

Intensity:

20-100 mW

Wavelength:

488 nm



Particle sizing of aqueous polystyrene latex solutions

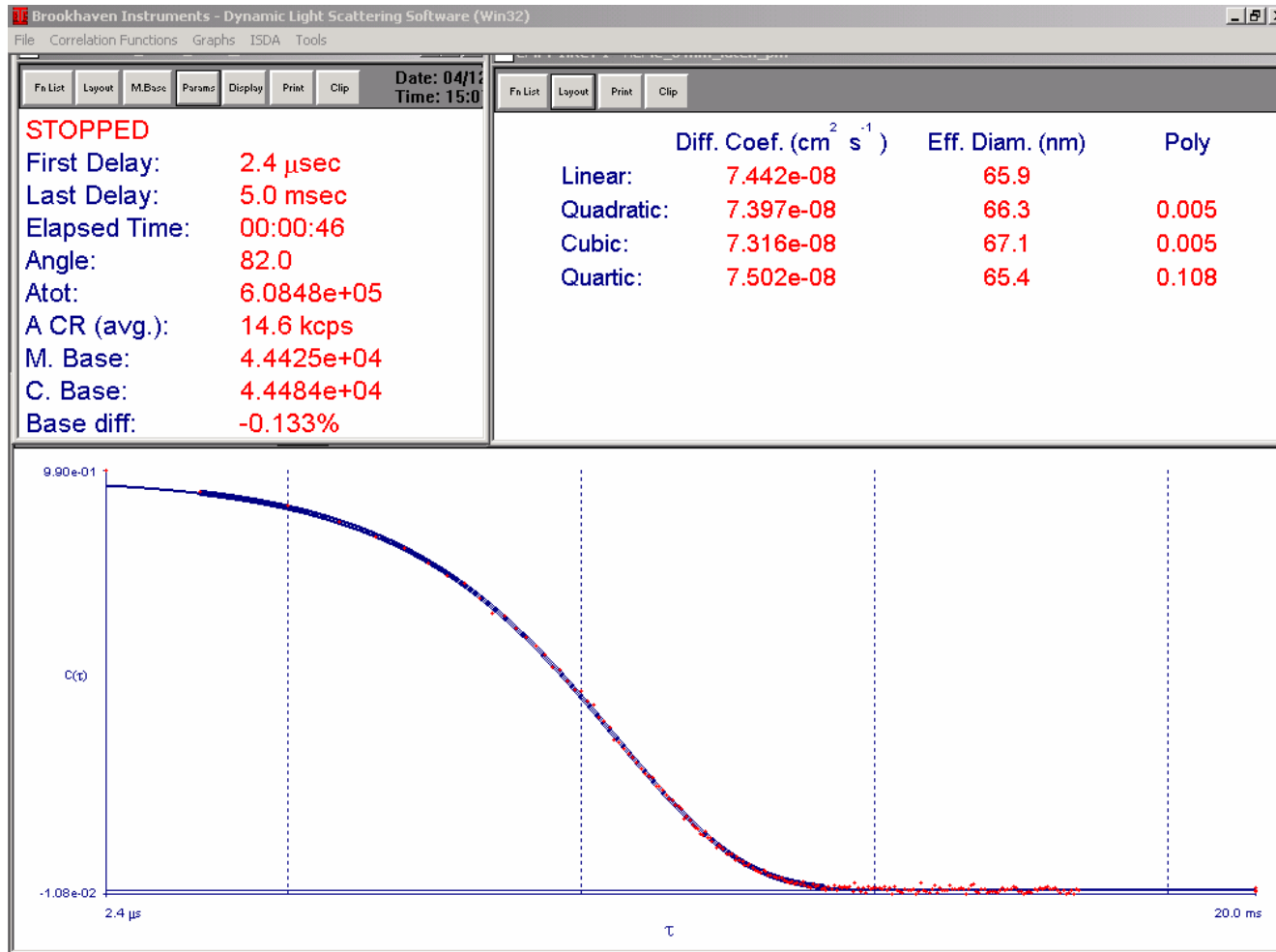
Manufacturer's size

Measured size

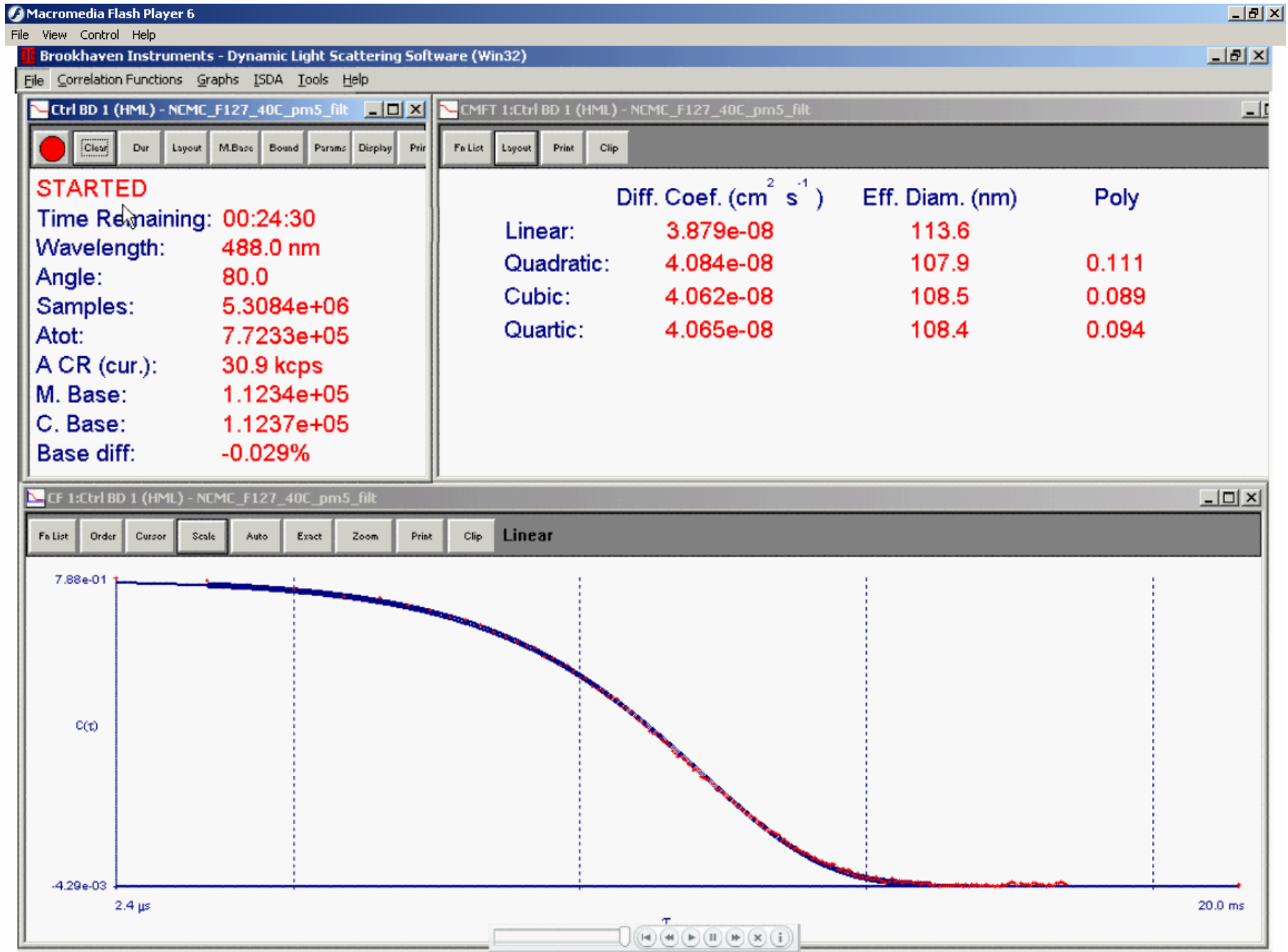
64 nm latex = 65 nm, poly 0.069

108 nm latex = 103 nm, poly 0.117

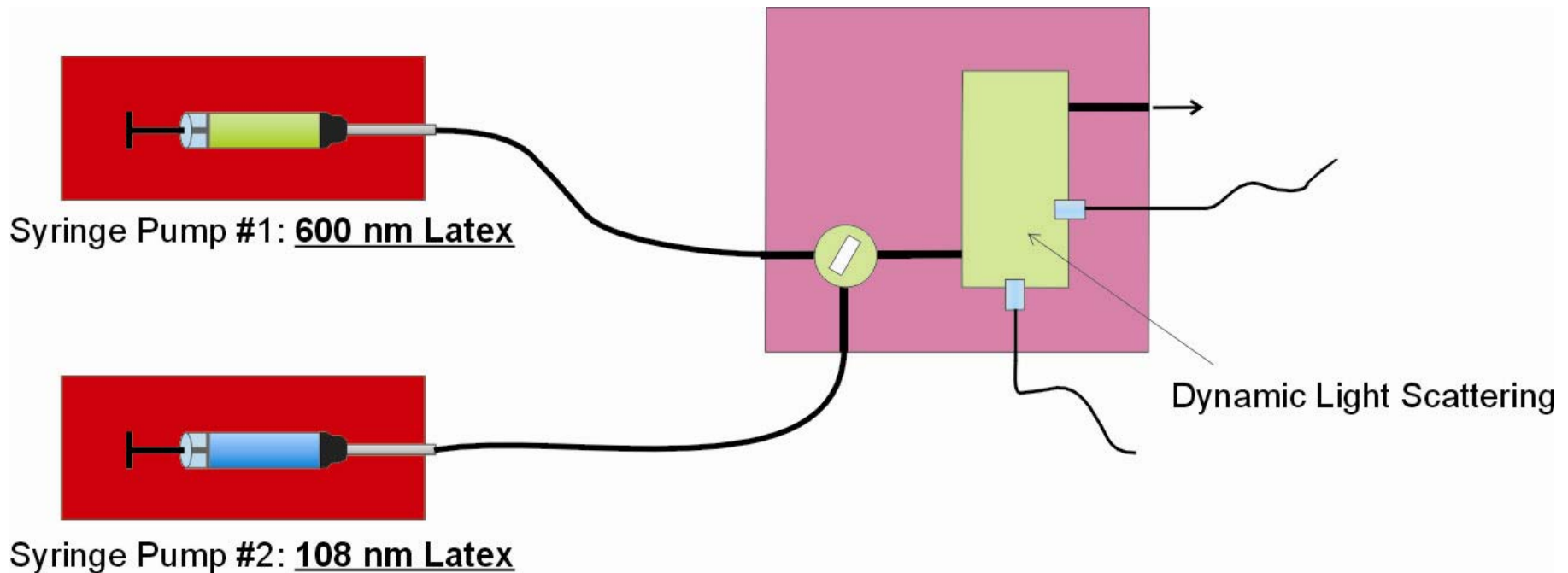
600 nm latex = 569 nm, poly 0.007



Example measurement of a 108 nm latex solution



Combined: particle sizing and sample flow



Overview of what will be demonstrated:

- The measurement chamber is initially filled with 600 nm latex solution
- A syringe pump is used to flow 108 nm solution into the chamber
- 135 μL are flowed over a 10 s period

These results will demonstrate the ability of this instrument to perform high throughput nanoparticle size measurements

Initially 600 nm latex, until 135 μ L of 108 nm latex pumped into measurement chamber

The screenshot displays two windows from a Macromedia Flash Player 6 environment. The top window is 'Brookhaven Instruments - Dynamic Light Scattering Software (Win32)'. It shows a 'STARTED' status and various parameters for a measurement. The bottom window is 'NoRamp2_Chastek.vi Front Panel', which is a LabVIEW interface for controlling syringe pumps.

Dynamic Light Scattering Software Parameters:

Parameter	Value
Time Remaining	00:24:43
Wavelength	488.0 nm
Angle	75.0
Samples	3.2440e+06
Atot	2.1090e+06
A CR (cur.)	140.7 kcps
M. Base	1.1435e+06
C. Base	1.1381e+06

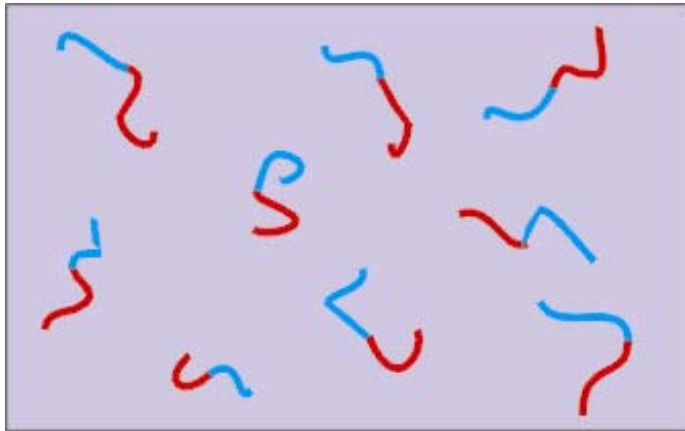
	Diff. Coef. ($\text{cm}^2 \text{s}^{-1}$)	Eff. Diam. (nm)	Poly
Linear:	6.555e-09	672.1	
Quadratic:	7.077e-09	622.6	0.202
Cubic:	7.423e-09	593.6	0.430
Quartic:	7.536e-09	584.7	0.540

NoRamp2_Chastek.vi Front Panel Parameters:

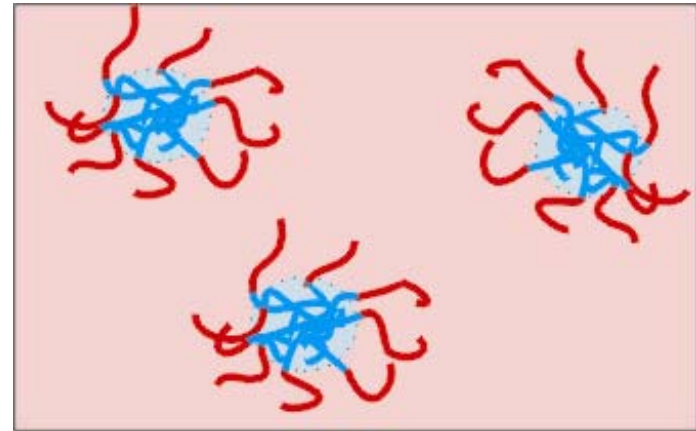
Pump Address	Syringe Diameter	Initial Rate	Rate A1-A4
Pump Address (A): 00	Syringe Diameter: 12.5	Initial Rate: 800 $\mu\text{L}/\text{min}$	Rate A2: 0 mL/min , Rate A3: 0 mL/min , Rate A4: 0 mL/min
Pump Address (B): 01	Syringe Diameter (b): 12.5	Initial Rate (b): 0 $\mu\text{L}/\text{min}$	Rate B2: 0 mL/min , Rate B3: 0 mL/min , Rate B4: 0 mL/min
Pump Address (C): none	Syringe Diameter (c):	Initial Rate (c): 0 mL/min	Rate C2: 0 mL/min , Rate C3: 0 mL/min , Rate C4: 0 mL/min
Pump Address (D): none	Syringe Diameter (d):	Initial Rate (d): 0 mL/min	Rate D2: 0 mL/min , Rate D3: 0 mL/min , Rate D4: 0 mL/min

The LabVIEW front panel also includes a note: '*Note: The lowest pump rate is about 10 $\mu\text{L}/\text{hr}$, and max is about 10 mL/min .' and a 'Tools' palette on the right side.

Altering solvent composition to dissolve block copolymer micelles

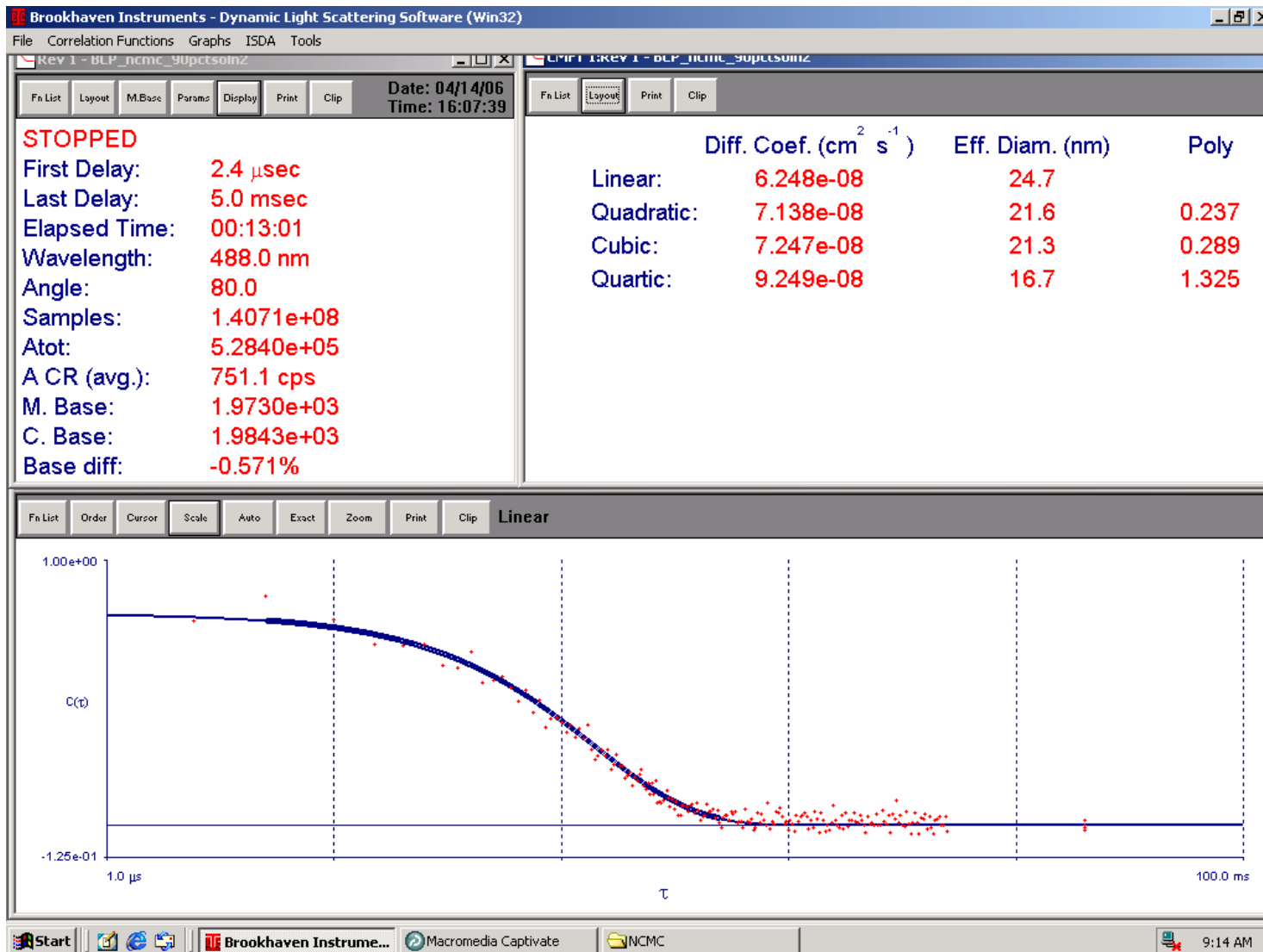


Unimer state in neutral
solvent (e.g., toluene)



Micelles form in selective
solvents (e.g., hexadecane)

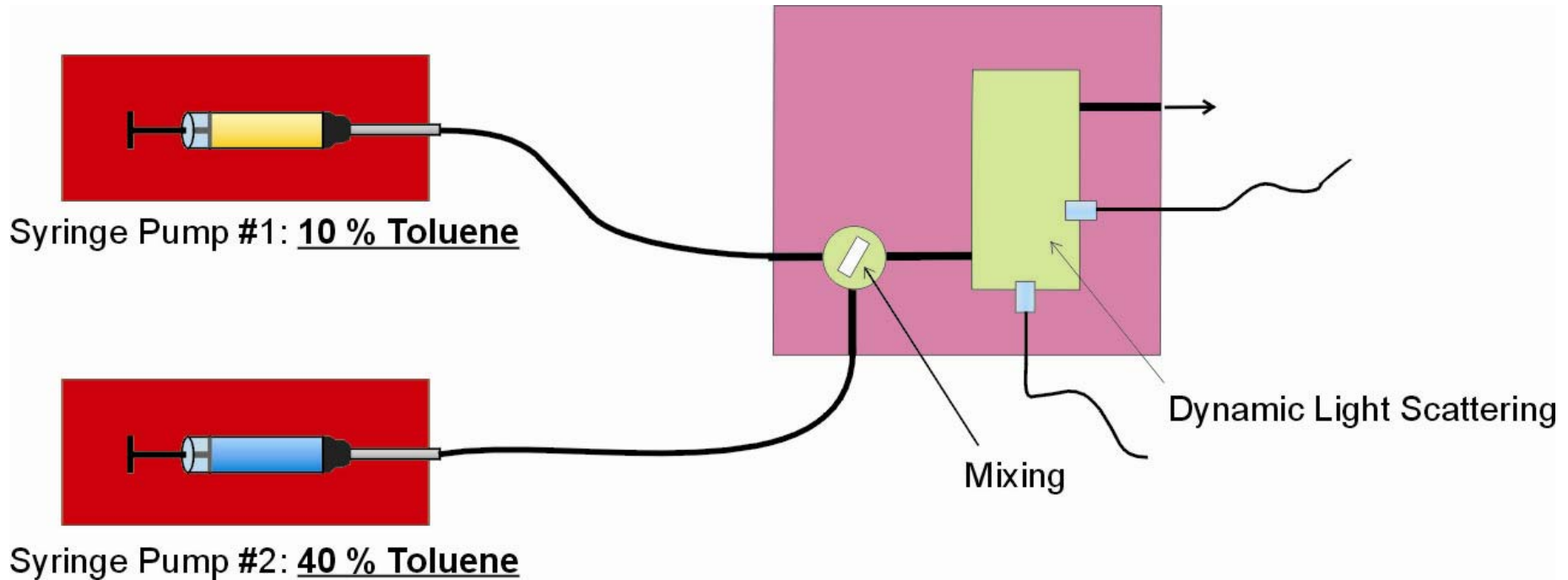
- polyisoprene corona
polystyrene core



PS-b-PI, symmetric, 20 kg/mol
 2% polymer, 10% toluene, 88% hexadecane

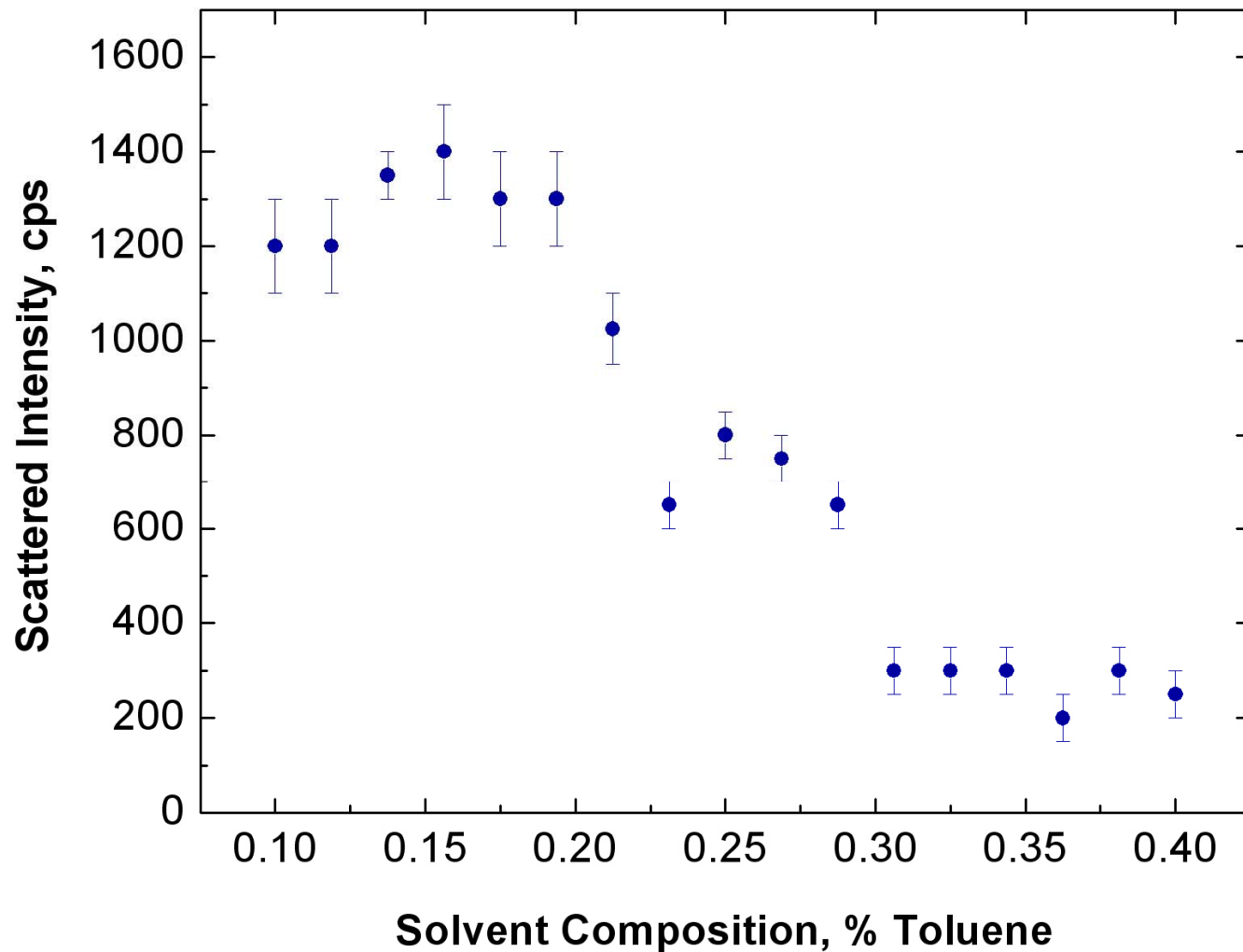
~ 21 nm micelles form

Experimental setup for flowing block copolymer solutions



Measurements are made by flowing each solution at **0-80 $\mu\text{L}/\text{min}$** for **2 min**, giving a volume of **160 μL**

e.g., when both are flowed at 40 $\mu\text{L}/\text{min}$, the blended sample will have 25% toluene



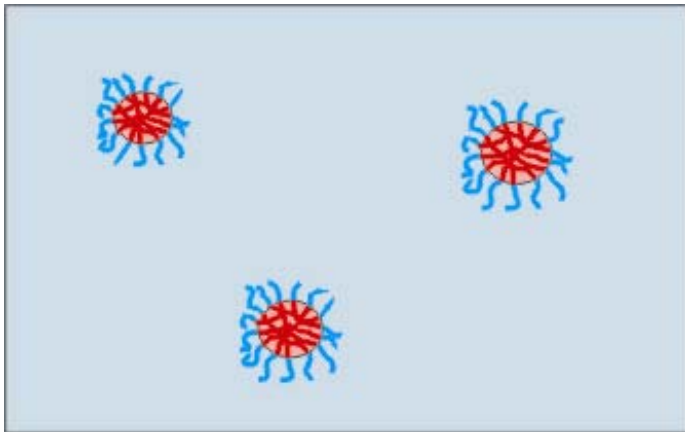
At 22 °C, PS-b-PI micelles dissociate in hexadecane/toluene if the solvent is composed of **22-28% toluene**.

- Each data point required only 160 μ L of solution

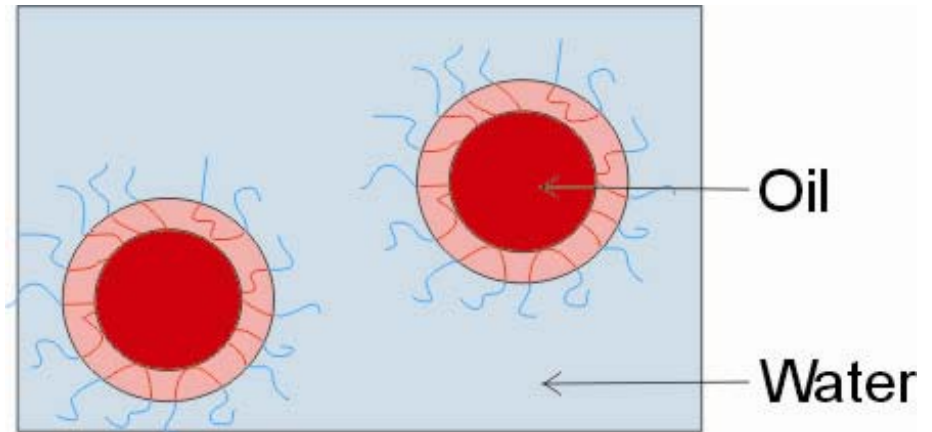
Block copolymer – Oil – Water equilibration



Poly(ethylene oxide-b-propylene oxide-b-ethylene oxide)



In pure water, pluronic polymers form micelles (at elevated temperature)

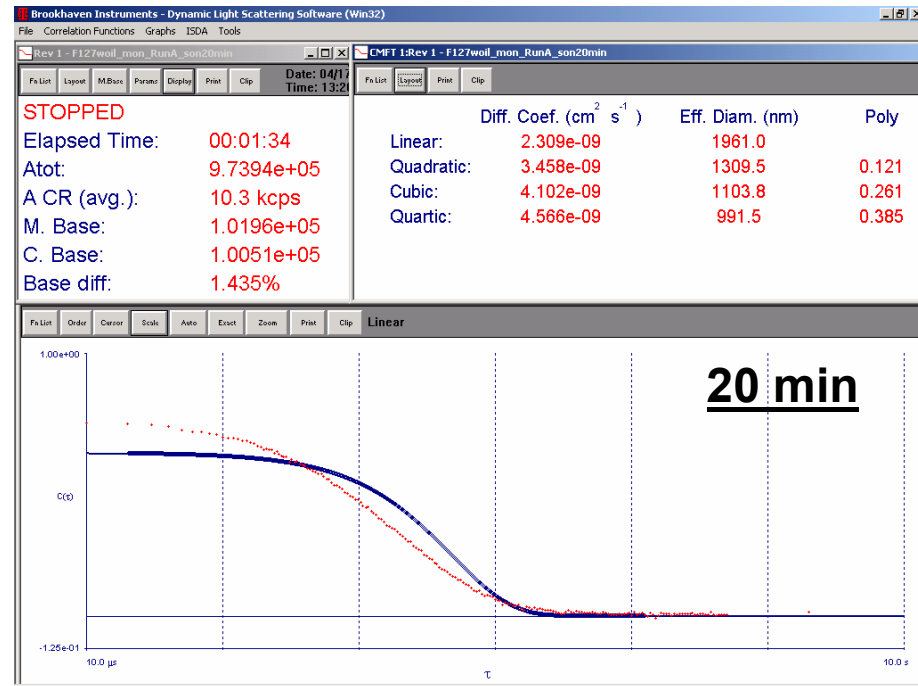
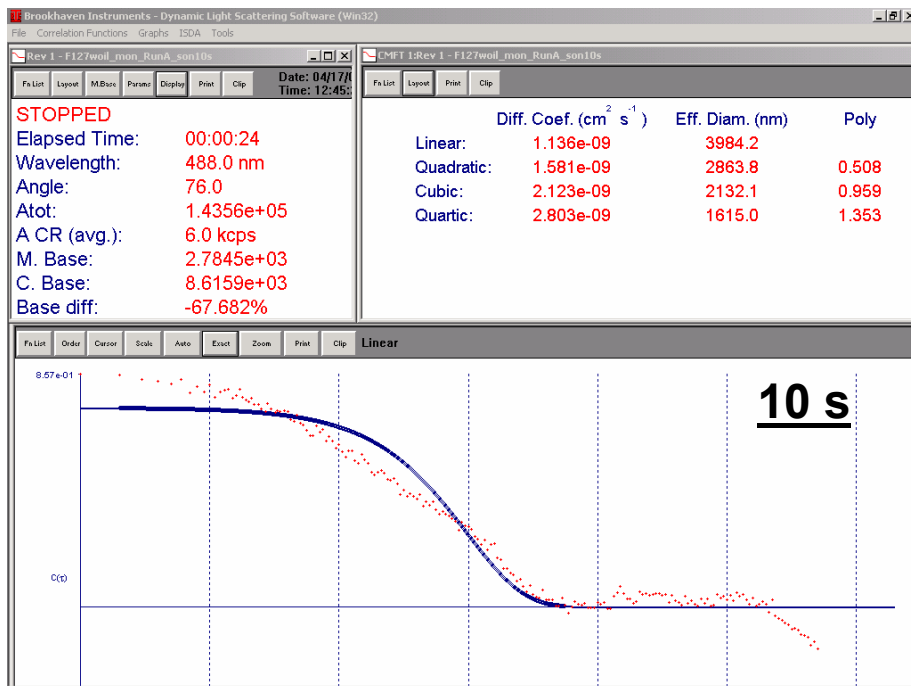
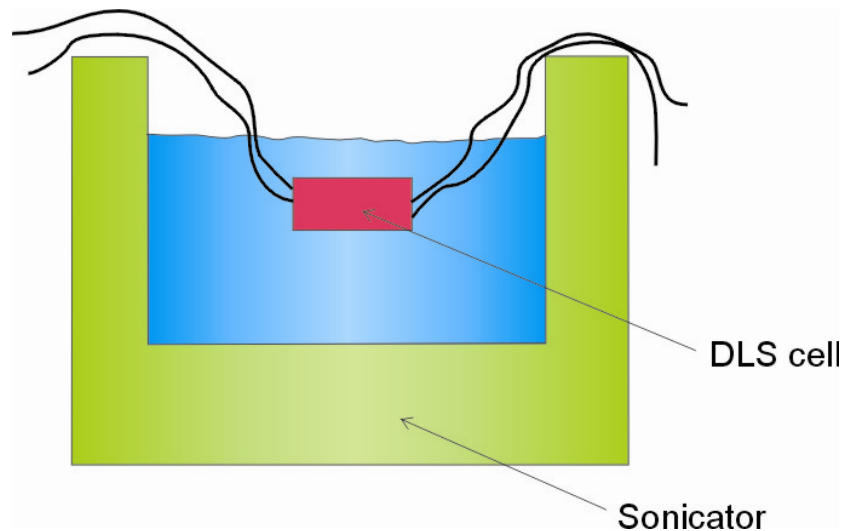


Added oil forms an emulsion
2% polymer, 1% oil, 97% water

The emulsion particle size is several hundred nanometers, but equilibrating the solution requires appropriate mixing

How to equilibrate – Sonication? **No.**

DLS cell was submerged under water in a sonicator to allow for *in situ* particle sizing.

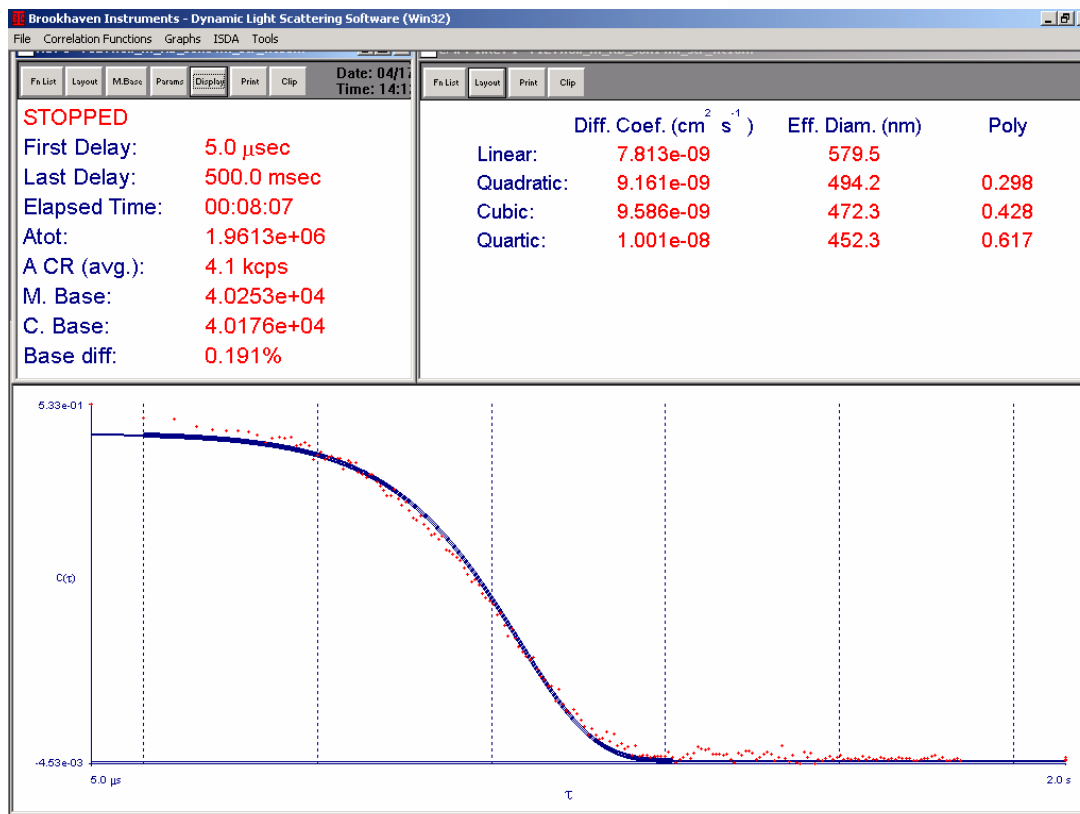
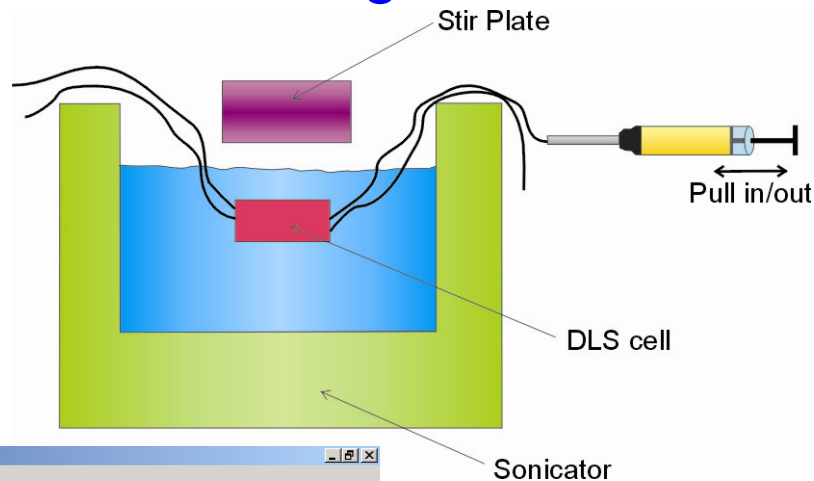


Particle size is broadly distributed even after 20 min of sonication

How to equilibrate – Sonication & Mixing? **Yes.**

Sonicating & mixing with a stir bar

- The sample is repeatedly pulled/pushed through the mixing chamber with a syringe
- 14 min of sonication and mixing gives a uniform particle size of ca. 500 nm



Summary

Fully operational microfluidic dynamic light scattering instrument has been made

- Demonstrated quantitative particle sizing from 20-600 nm on timescales as short as 5 s in both organic and aqueous solutions
- Demonstrated particle sizing of a 135 μL aliquot of sample flowed into the measurement chamber
- Demonstrated solution blending to determine the affect of solvent composition on micelle formation
- Demonstrated *in situ* sonication and mixing as a means to equilibrate an oil-water-block copolymer emulsion

Future improvements

- Accurate temperature control
- Reduction in volume
- Multi-angle measurements

Demo in room B223