Microfluidic Dynamic Light Scattering

Tom Chastek
Traditional dynamic light scattering instrument
Traditional DLS instrument
– TOP VIEW

Microfluidic DLS instrument

Optical Fibers with microlenses embedded directly into the sample
**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

**Microlens:** 1 mm diameter, 3.1 mm long

**Fiber optic:** overall – 254 µm  
active area - ~5 µm
Fiber optic probe with microlens

Beam divergence at 3 meters

Beam diameter: 400 µm
Intensity: 20-100 mW
Wavelength: 488 nm

Red helium-neon laser used as reference
Particle sizing of aqueous polystyrene latex solutions

<table>
<thead>
<tr>
<th>Manufacturer’s size</th>
<th>Measured size</th>
</tr>
</thead>
<tbody>
<tr>
<td>64 nm latex</td>
<td>65 nm, poly 0.069</td>
</tr>
<tr>
<td>108 nm latex</td>
<td>103 nm, poly 0.117</td>
</tr>
<tr>
<td>600 nm latex</td>
<td>569 nm, poly 0.007</td>
</tr>
</tbody>
</table>

**Table with Results:**

<table>
<thead>
<tr>
<th></th>
<th>Diff. Coef. (cm² s⁻¹)</th>
<th>Eff. Diam. (nm)</th>
<th>Poly</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>7.442e-08</td>
<td>85.9</td>
<td></td>
</tr>
<tr>
<td>Quadratic</td>
<td>7.397e-08</td>
<td>86.3</td>
<td>0.005</td>
</tr>
<tr>
<td>Cubic</td>
<td>7.316e-08</td>
<td>87.1</td>
<td>0.005</td>
</tr>
<tr>
<td>Quartic</td>
<td>7.502e-08</td>
<td>65.4</td>
<td>0.108</td>
</tr>
</tbody>
</table>

**Graph showing the size distribution of latex solutions.**
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 µL of 108 nm latex pumped into measurement chamber.
Altering solvent composition to dissolve block copolymer micelles

Poly(styrene-b-isoprene)

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 $\mu$L/min for 2 min, giving a volume of 160 $\mu$L.

e.g., when both are flowed at 40 $\mu$L/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 μL of solution
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.
DLS cell was submerged under water in a sonicator to allow for *in situ* particle sizing.

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

Particle size is broadly distributed even after 20 min of sonication.
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 µm

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### Table: Diff. Coef. & Eff. Diam.

<table>
<thead>
<tr>
<th>Type</th>
<th>Diff. Coef. (cm² s⁻¹)</th>
<th>Eff. Diam. (nm)</th>
<th>Poly</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>7.813e-09</td>
<td>579.5</td>
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<tr>
<td>Quadratic</td>
<td>9.161e-09</td>
<td>494.2</td>
<td>0.289</td>
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<tr>
<td>Cubic</td>
<td>9.589e-09</td>
<td>472.3</td>
<td>0.429</td>
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<tr>
<td>Quartic</td>
<td>1.001e-08</td>
<td>452.3</td>
<td>0.617</td>
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</tbody>
</table>

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### Diagram: Dynamic Light Scattering Analysis

- **Stir Plate**: Movement of the sample
- **Pull in/out**: Direction of the syringe
- **DLS cell**: Container for scattering analysis
- **Sonicator**: Source of ultrasonic energy

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