

Monolith-Based Electroosmotic Pump (EOP)

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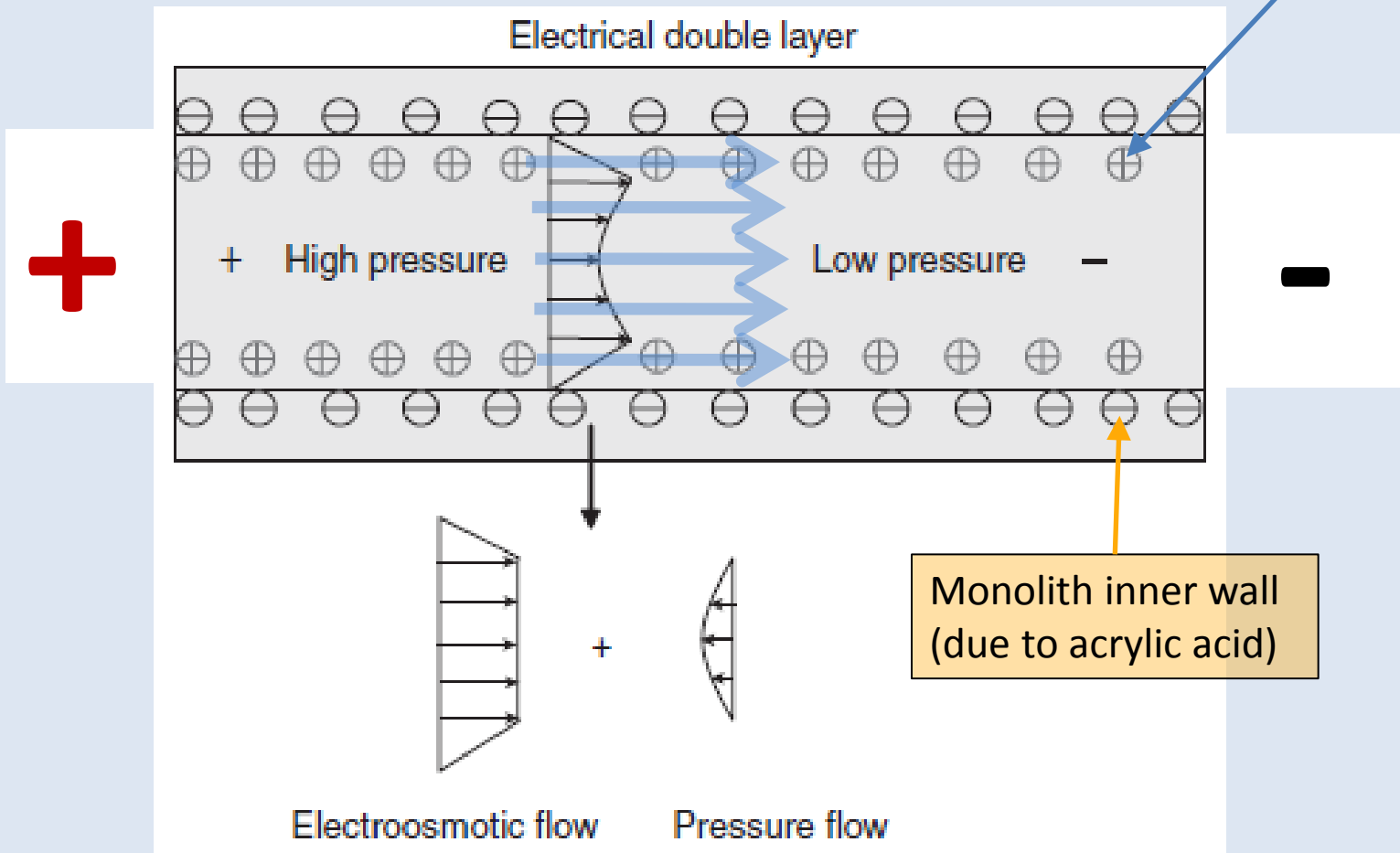
Background

- **Electroosmosis:** bulk motion of electrolyte caused by electric forces acting on regions of net charge in a microchannel¹.
- **Electroosmotic pumps (EOP)** use electroosmosis to generate flow rate¹.

1. Yao, S, et al. (2003). Porous glass electroosmotic pumps: design and experiments. *Journal of Colloid and Interface Science*, 268, 143–153.

Background, cont.

Protonated fluid



Monolith inner wall
(due to acrylic acid)

Electroosmotic flow Pressure flow



Background, cont.

- **Advantages of EOP (vs. mechanical pump) ²:**
 - constant pulse-free flows
 - elimination of moving parts
 - uses common materials and fabrication methods.

2. Wang, X, et al. (2009). Electroosmotic pumps and their applications in microfluidic systems. *Microfluid Nanofluidics*, 6(2), 145-162.

Background, cont.

The diagram shows the equation for electroosmotic flow rate, $Q_{eo} = \frac{n \epsilon \zeta V w d}{4 \pi \eta L}$. Annotations include:

- EO Flow Rate**: A yellow box pointing to the Q_{eo} term on the left.
- Cross Sectional Area**: A white box with blue arrows pointing to the $w d$ term in the numerator.
- Pump Geometry**: A yellow box with blue arrows pointing to the $w d$ term in the numerator and the L term in the denominator.
- Length**: A white box with a blue arrow pointing to the L term in the denominator.
- Related to buffer**: A yellow box with orange arrows pointing to the n and η terms.

Variables are highlighted with colored boxes: n and $w d$ are in red circles; ϵ and η are in blue boxes; L is in a red circle.



Project Goal

- **Develop** a disposable EOP with:
 - small size
 - low operating voltage
 - easy fabrication for mass production
- **Optimize** the operating conditions, including:
 - voltage
 - running buffer



Project Approach

- Polymer monolith-based EOP:
 - Acrylamide (APN)-based monolith
 - Butyl Methacrylate (BMA)-based monolith



Project Approach

- Polymer monolith-based EOP:
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APN-Based Monolith

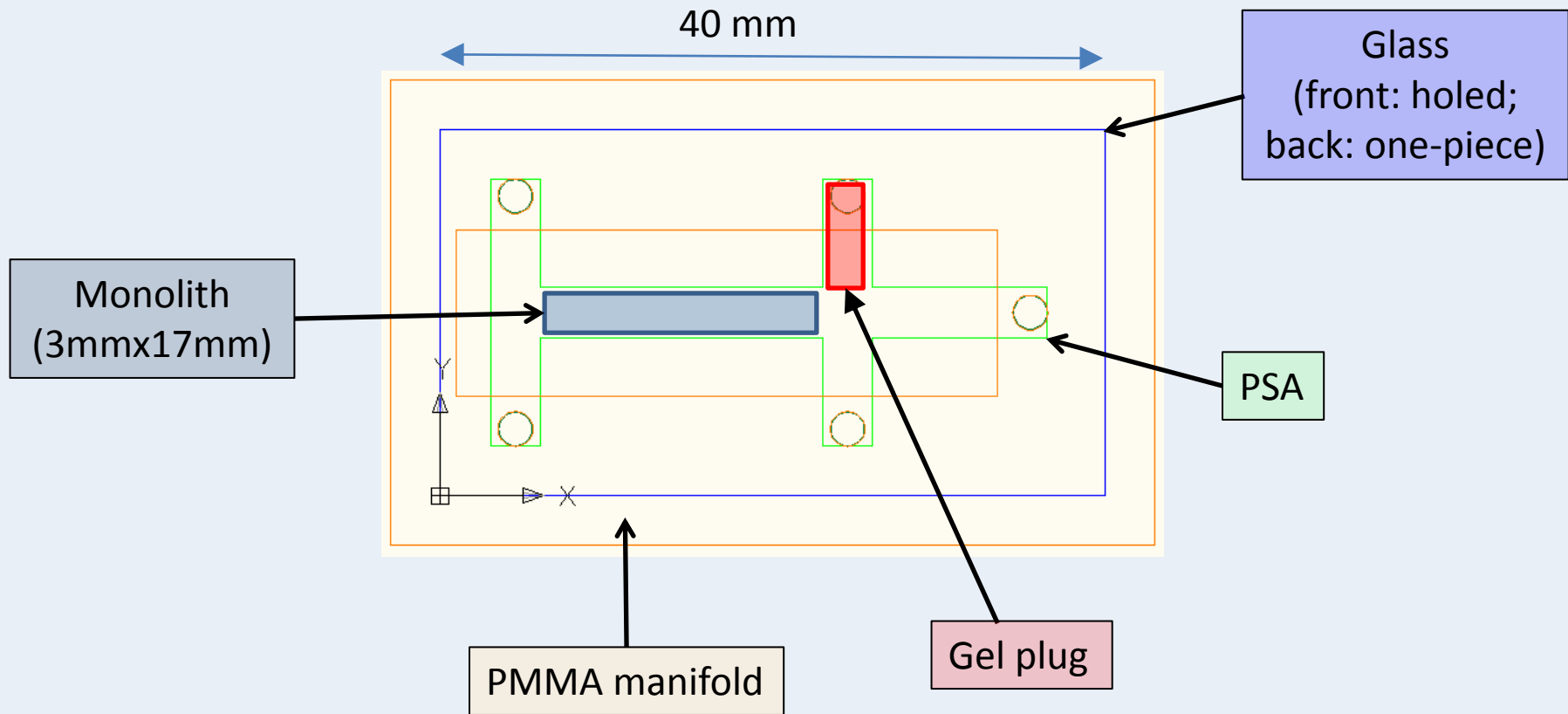
- APN acronym: **A**crylamide-**P**DA-**N**MF
 - Free radical polymerization
- Monolith **composition**:
 - 40% Acrylamide in 20x Borate (backbone)
 - PDA: N,N'-diacryloylpiperazine (cross-linker)
 - NMF: N-methylformamide (porogen)



APN-Based Monolith, cont.

- Monolith **composition**, cont.:
 - Polyethylene glycol (PEG) 8000
(Aggregates H₂O and hydrophilic monomers, pore enlarger)
 - VA-086 (Photoinitiator)
- For Negatively Charged Monolith, also add:
 - Acrylic acid

EOP Chip Design

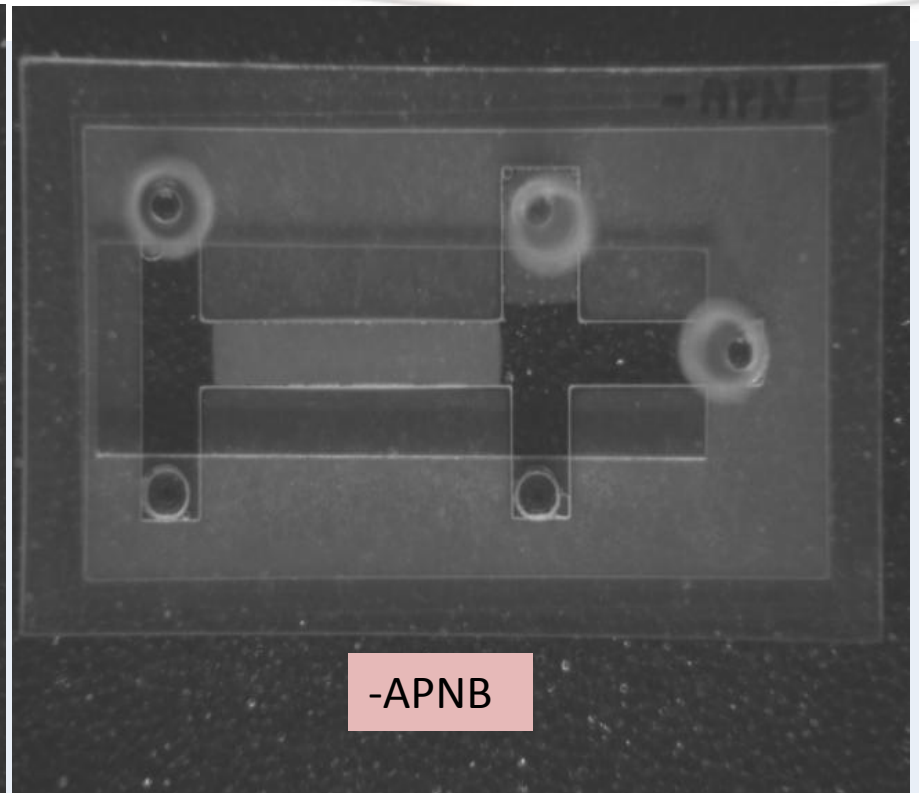
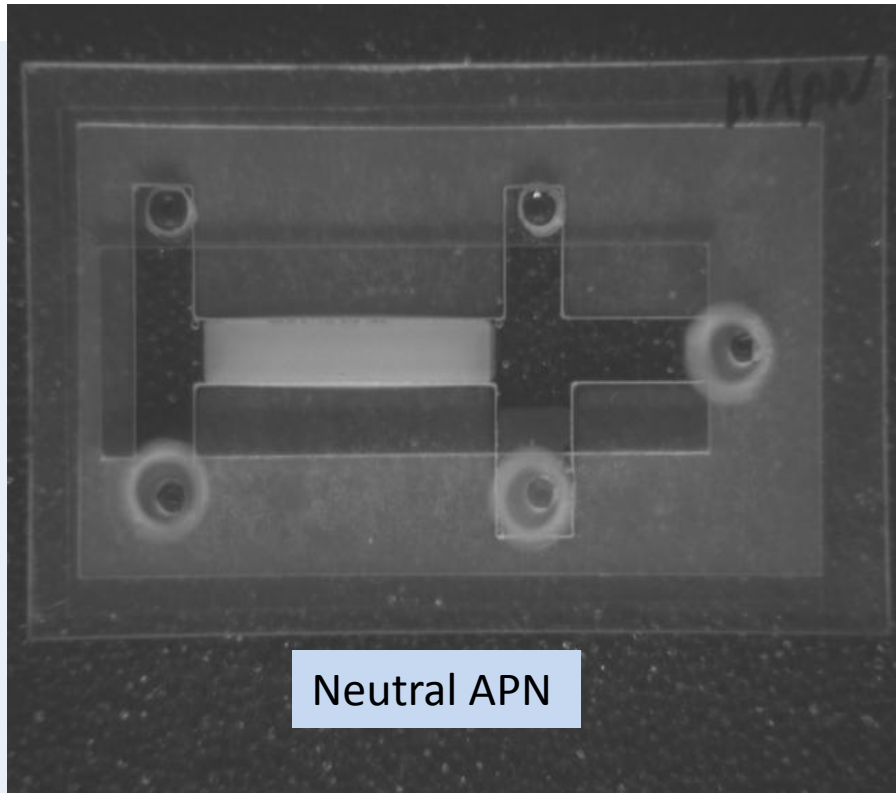




Monolith Fabrication Protocol

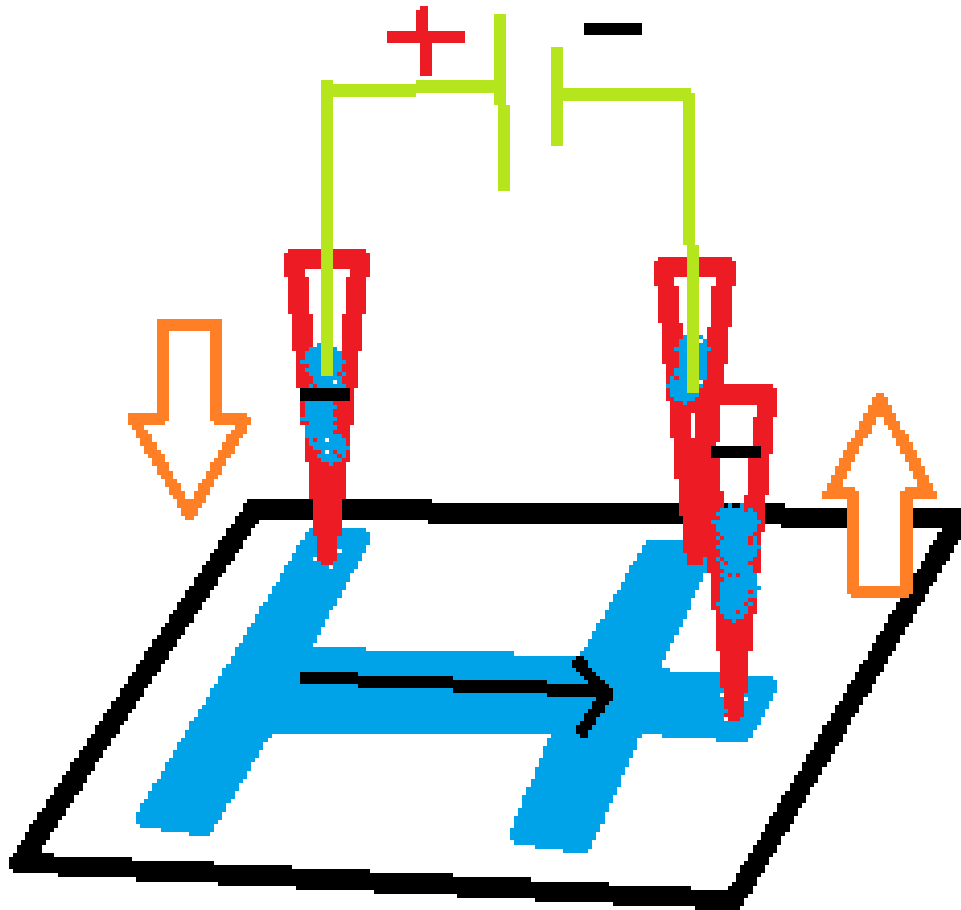
1. Assemble EOP chip
2. Treat chip channels with silane solution to create better adhesion of monolith polymer
3. Add monomer mixture, place mask around monolith area, and UV for 100s
4. Add gel plug mixture, place mask around gel plug area and UV for 50s

Photos: APN-Based Monolith



-APN Borate (**-APNB**) monolith (with acrylic acid) is more **transparent** and **gel-like** (smaller pores) than **neutral APN**, which is more monolith-like (bigger pores).

Experiment Set-up





Experiments

Find the optimal...

1. Voltage to run EOP
2. Polymerization condition
3. Running buffer



Experiments

Find the optimal...

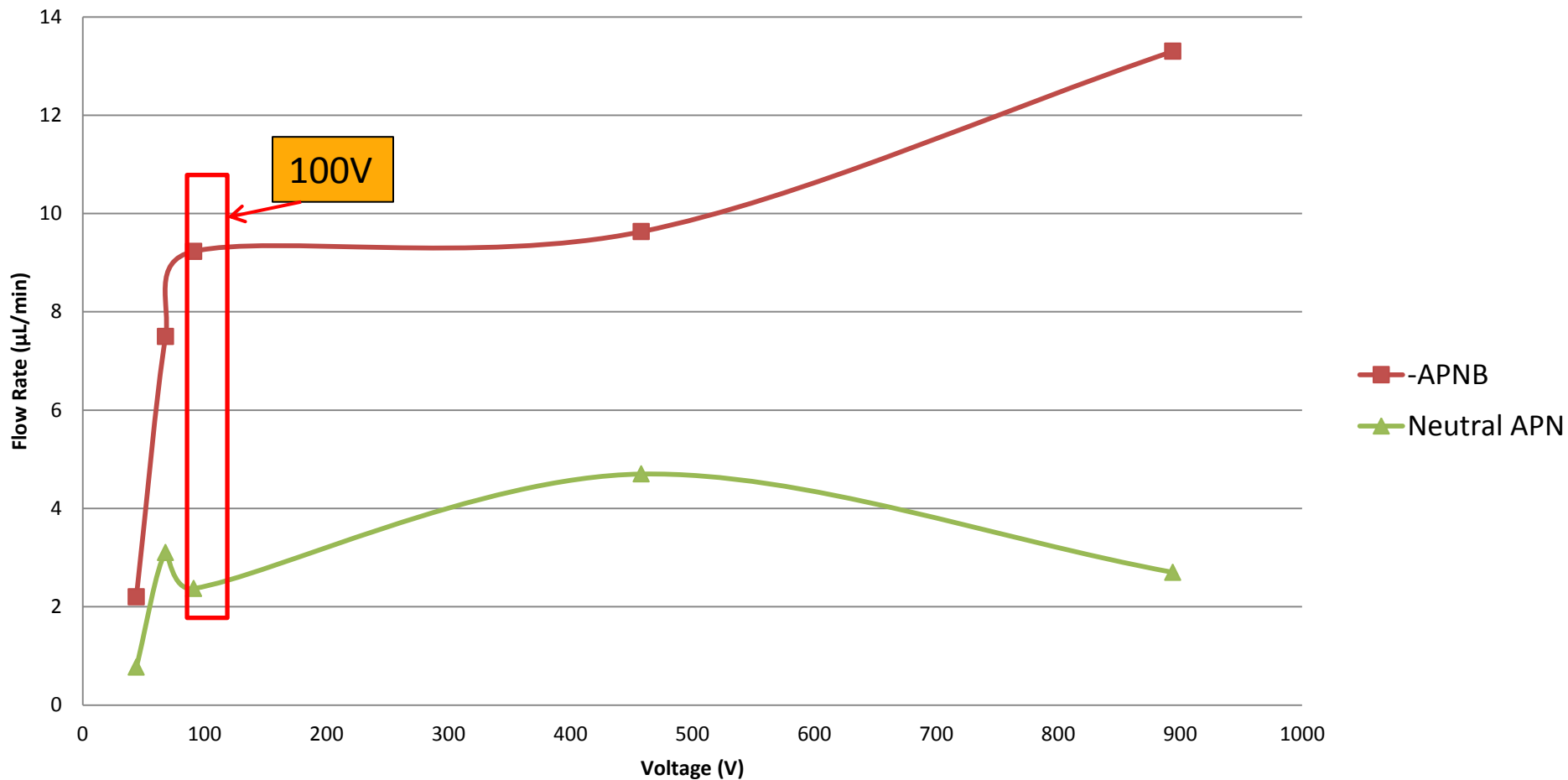
1. Voltage to run EOP

- **50V**
- **75V**
- **100V**
- **500V**
- **1000V**

2. Polymerization condition

3. Running buffer

Flow Rate – Voltage Correlation: APN Monolith



Flow Rate (µL/min)		
Voltage	-APNB	Neutral APN
44	2.2	0.77
68	7.5	3.1
91	9.23	2.37
458	9.63	4.7
894	13.3	2.7
* all were ~100 µA		



Optimal Voltage to Run EOP

- 50V → 100V: **linear** flow response
- Flow rate **past 100V** not a significant increase
 - Portable devices use voltages **under 100V**
- THUS: For high flow rate at low voltage, **100V** is optimal
 - For experiments, test 50V, 75V, and 100V



Experiments

Find the optimal...

1. Voltage to run EOP

- 50V
- 75V
- 100V
- 500V
- 1000V

2. Polymerization condition

3. Running buffer



Experiments

Find the optimal...

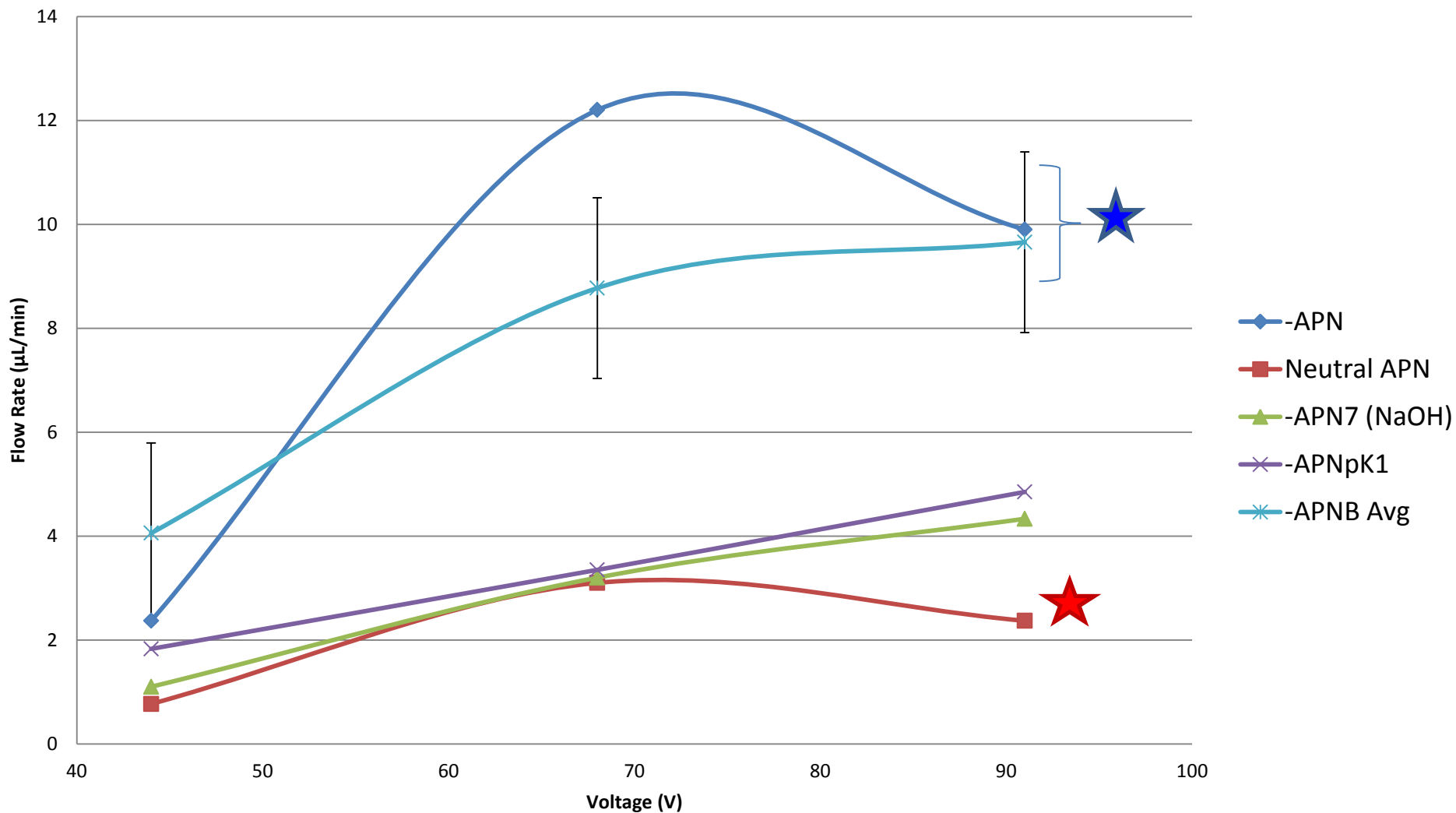
1. Voltage to run EOP

2. Polymerization condition


- **-APN** (H₂O)
- **-APNB** (pH 9)
- **-APN7** (pH 7)
- **-APNpK1** (pK 1)

3. Running buffer

Flow Rate for Variable Polymerization Conditions (pH)



Flow Rate (µL/min)					
Voltage	-APN	Neutral APN	-APN7	-APNpK1	-APNB
44	2.37	0.77	1.1	1.83	4.06
68	12.2	3.1	3.2	3.35	8.77
91	9.9	2.37	4.33	4.85	9.66
* all were ~100 µA					



Optimal Polymerization Condition, cont.

- Both -APN and -APNB produce high flow rate over voltage range (50-100V).
- BUT –APNB:
 - more **consistent** results
 - better **linearity**
 - more **stable**
- THUS:
Choose **-APNB** as optimal polymerization condition



Experiments

Find the optimal...

1. Voltage to run EOP

2. Polymerization condition

- -APN
- -APNB
- -APN7
- -APNpK1

3. Running buffer



Experiments

Find the optimal...

1. Voltage to run EOP
2. Polymerization condition

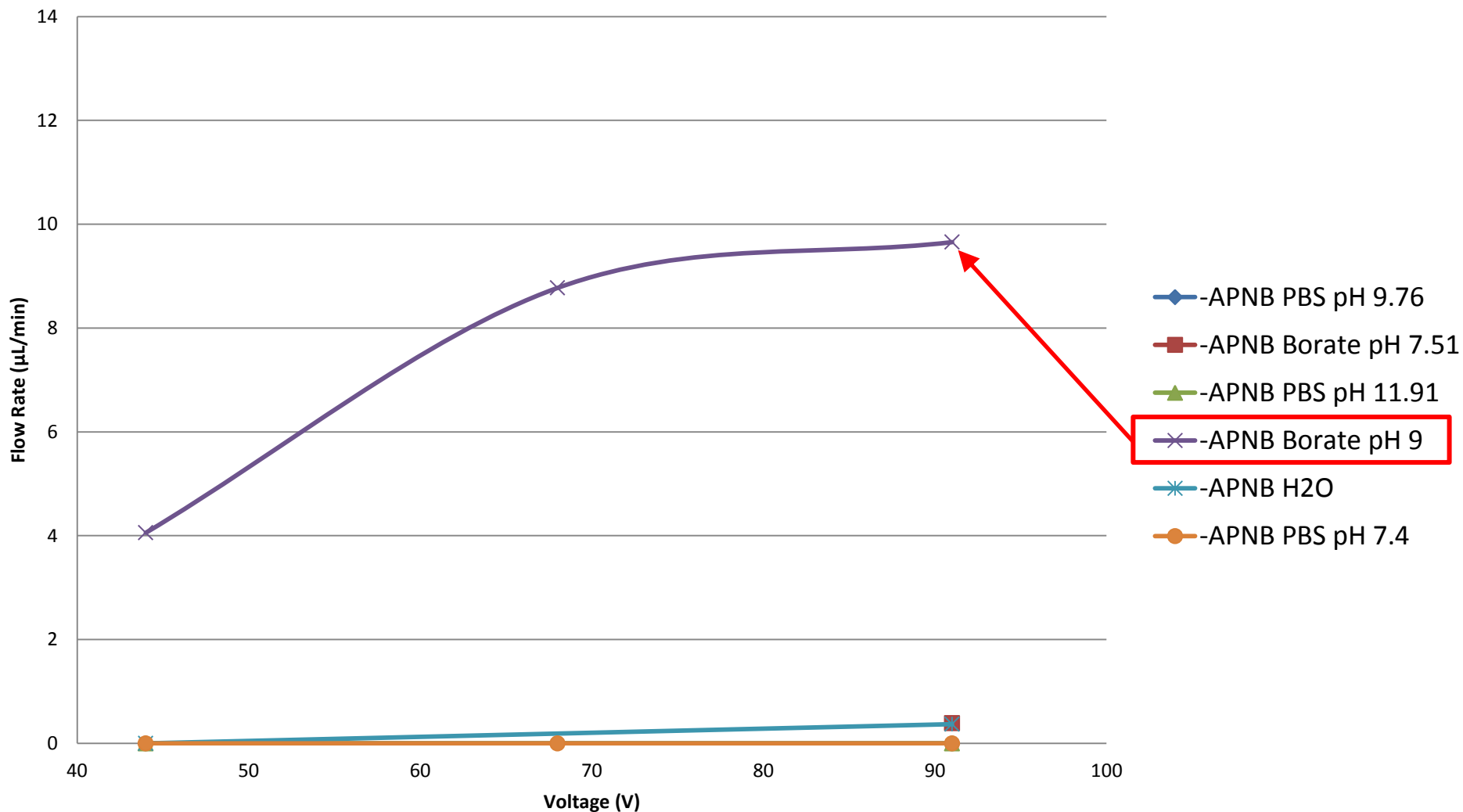
3. Running buffer

- **Borate**
 - pH 9
 - pH 7.51 (adjusted)
- **PBS**
 - pH 7.2
 - pH 9.76 (adjusted)
 - pH 11.91 (adjusted)

Optimal Running Buffer

- **Borate:** 50 mM Borate + 1 mM NaCl
 - effective running buffer for EOP in literature
 - BUT it *cannot* be used directly in immunoassays
- **PBS :** 10mM Na Phosphate + 150 mM NaCl
 - commonly used in immunoassays
- THUS, if EOP used PBS, it could be directly connected to the downstream immunoassay

Flow Rate for Variable Running Buffers



Flow Rate (µL/min)						
Voltage	-APNB PBS pH 9.76	-APNB Borate pH 7.51	-APNB PBS pH 11.91	-APNB Borate pH 9	-APNB H2O	-APNB PBS pH 7.4
44	0		0	4.06	0	0
68				8.77		0
91	0	0.39	0	9.66	0.37	0

* all PBS were ~50 µA and Borate was ~60 µA except for Borate 9 (~100 µA)



Optimal Running Buffer, cont.

- **Borate** running buffer at unmodified pH 9 produces optimal flow rate
- **PBS** buffer and **lower pH (<9)** are not able to produce significant flow
- **THUS: Borate pH 9** running buffer is optimal




Experiments

Find the optimal...

1. Voltage to run EOP
2. Polymerization condition

3. Running buffer

- **Borate**
 - pH 9
 - pH 7.51 (adjusted)
- **PBS**
 - pH 7.2
 - pH 9.76 (adjusted)
 - pH 11.91 (adjusted)



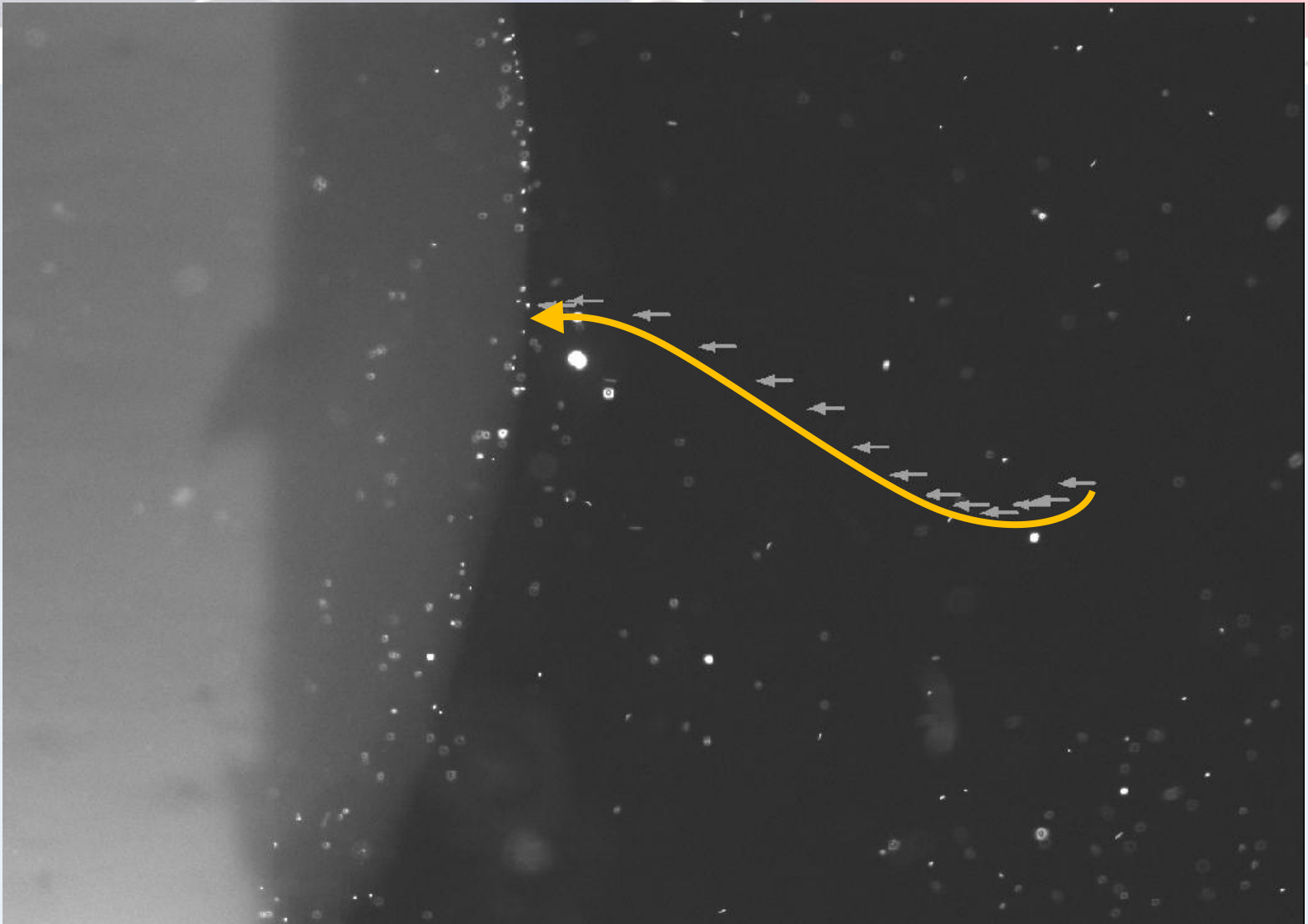
Optimization of EOP Summary

- Optimal:
 - Voltage: 100V
 - Polymerization: -APNB (Borate)
 - Running buffer: Borate 20x + NaCl
- **Next Step:** Visualize flow to ensure fluid moves **through** vs. around monolith
 - Green fluorescent beads 1 μm
 - Inverted fluorescent microscope

Fluorescent Visualization of Flow



Visualization of Flow Direction





Problems with APN-Based Monolith

- **Stability** of monolith
- **Consistency** of flow rate
 - Variables: incubation time, number of runs
- **Controllability** of flow rate
 - More linear flow rate-voltage correlation needed
- **Higher** flow rate desired



Project Approach

- Polymer monolith-based EOP:
 - Acrylamide (APN)-based monolith
 - Butyl Methacrylate (BMA)-based monolith

BMA-Based Monolith

- BMA acronym: **B**utyl **M**eth**A**crylate
- **Living-radical polymerization (LRP)**: radicals can be initiated or deactivated in a reversible way³
 - Allows grafting of different monolith layers
 - TED: **T**etra**E**thylthiuram **D**isulfide
- Goal: graft acrylic acid on outer monolith side via LRP, to avoid pore blockage



BMA-Based Monolith, cont.

- Monolith **composition**:
 - Butyl methacrylate (backbone)
 - EGDMA: Ethylene glycol dimethacrylate (cross-linker)
 - Methanol (porogen)



BMA-Based Monolith, cont.

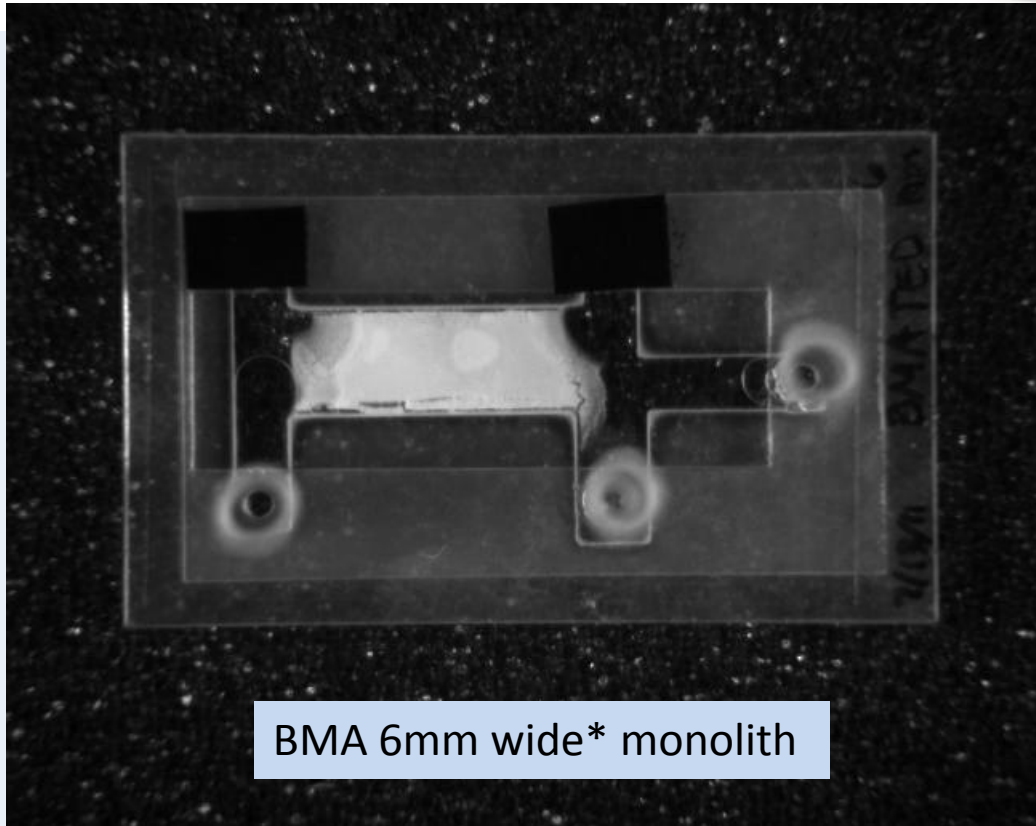
- Monolith **composition**, cont:
 - TED (chain terminator agent)
 - DMPA: 2,2-dimethoxy-2-phenyl acetophenone (photoinitiator)
- For Negatively Charged Monolith, also add:
 - Acrylic acid
 - Grafted after monolith polymerization



BMA Monolith Fabrication Protocol

1. Assemble EOP chip
2. Treat chip channels with silane solution
3. Add monomer mixture into channels, place mask over monolith area, and **UV for 300s**
4. Add gel plug mixture, place mask over gel plug area and UV for 50s
5. Add acrylic acid + 40% PEG acrylate 375 mixture and repeat step 3, but **UV for 30s**

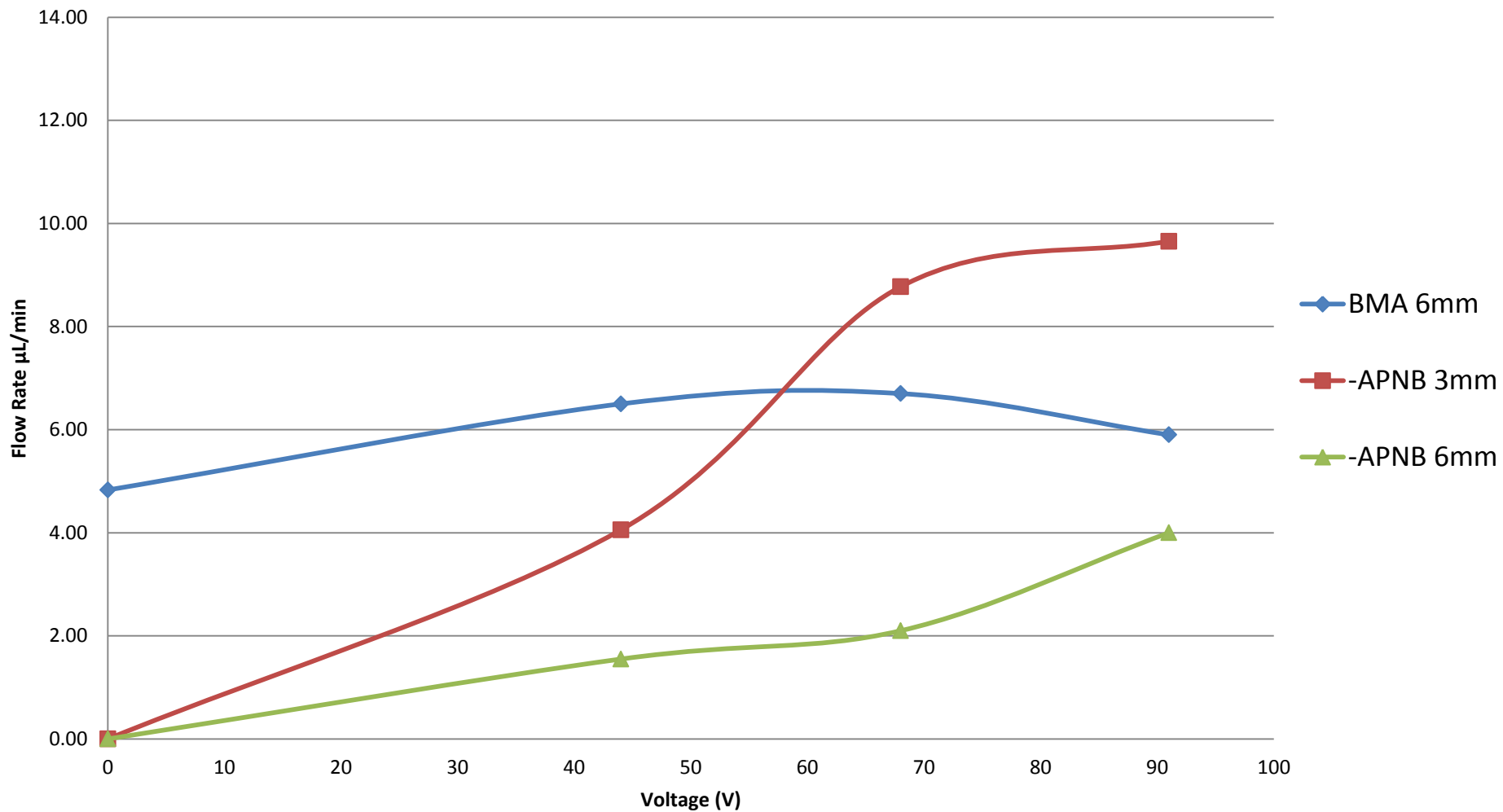
Photo: BMA-Based Monolith



BMA 6mm wide* monolith

*NOTE: monolith width was increased (doubled) to decrease resistance

Flow Rate-Voltage Correlation: BMA Monolith



Flow Rate (µL/min)			
Voltage	BMA 6mm	-APNB 3mm	-APNB 6mm
0	4.83	0.00	0
44	6.50	4.06	1.55
68	6.70	8.77	2.1
91	5.90	9.66	4

* all were ~100 µA



Problems with BMA-Based Monolith

- **Grafting** of acrylic acid
 - Not grafting
 - Clogged pores
 - Overpolymerization or Monomer residue
- **Consistency** of flow rate
- **Controllability** of flow rate
- **Higher** flow rate desired



Conclusions

- Acrylamide (APN)-based monolith EOP:
 - Can provide **9.66 $\mu\text{L}/\text{min}$** flow rate **under 100 V**
 - Optimum running buffer is **Borate**
 - Size of monolith is 3mm x 17 mm (**small size**)
- Existing **problems**:
 - Unstable monolith
 - Inconsistent flow rate
 - Low controllability of flow rate



Conclusions, cont.

- Butyl Methacrylate (BMA)-based monolith EOP:
 - Similar to APN-based monolith optimization
 - Sturdier monolith
 - Has grafting ability
- Existing **problems:**
 - Shallow flow rate increase over voltage range
 - 3mm wide BMA-based monolith clogs
 - Low controllability and inconsistency of flow rate

Meeting Project Goals

- **Develop** a disposable EOP with:
 - small size Monolith: 3mm x 17mm
 - low operating voltage Under 100V
 - easy fabrication for mass production PMMA, glass, PSA, monolith
- **Optimize** the operating conditions, including:
 - voltage Up to 100V
 - running buffer Borate



Future Directions

- Explore possibility of glass fiber EOP
- Explore other polymer-based monoliths
 - BMA with better grafting conditions
- Redesign EOP for higher flow rates
- Integration of EOP with downstream on-chip immunoassay

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