

REPORT DOCUMENTATION PAGE

PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.

1. REPORT DATE 20210920	2. REPORT TYPE Briefing Charts	3. DATES COVERED	
		START DATE 20210913	END DATE 20210930
4. TITLE AND SUBTITLE Fluoropolymers for Propellant Binders: Towards Energy-Dense Polymers for Solid Rocket Motors			
5a. CONTRACT NUMBER	5b. GRANT NUMBER	5c. PROGRAM ELEMENT NUMBER	
5d. PROJECT NUMBER	5e. TASK NUMBER	5f. WORK UNIT NUMBER Q2F1	
6. AUTHOR(S) Alexander Lonnecker & Kamran Ghiassi			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RQRP 10 E. Saturn Blvd EDWARDS AFB, CA 93524-7680			8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFRL/RQR 5 Pollux Drive Edwards AFB, CA 93524-7048		10. SPONSOR/MONITOR'S ACRONYM(S) AFRL/RQR	11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-RQ-ED-VG-2021-236
12. DISTRIBUTION/AVAILABILITY STATEMENT Distribution Statement A: Approved for Public Release; Distribution Unlimited. PA Clearance Number: AFRL-2021-3116; Clearance Date: 14 September 2021			
13. SUPPLEMENTARY NOTES For presentation at 2021 Dynamic Materials and Interactions Laboratory Task Review The U.S. Government is joint author of the work and has the right to use, modify, reproduce, release, perform, display, or disclose the work.			
14. ABSTRACT Viewgraph/Briefing Charts			
15. SUBJECT TERMS N/A			
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified	
			18. NUMBER OF PAGES 28
19a. NAME OF RESPONSIBLE PERSON Kamran Ghiassi			19b. PHONE NUMBER (Include area code) N/A



U.S. AIR FORCE

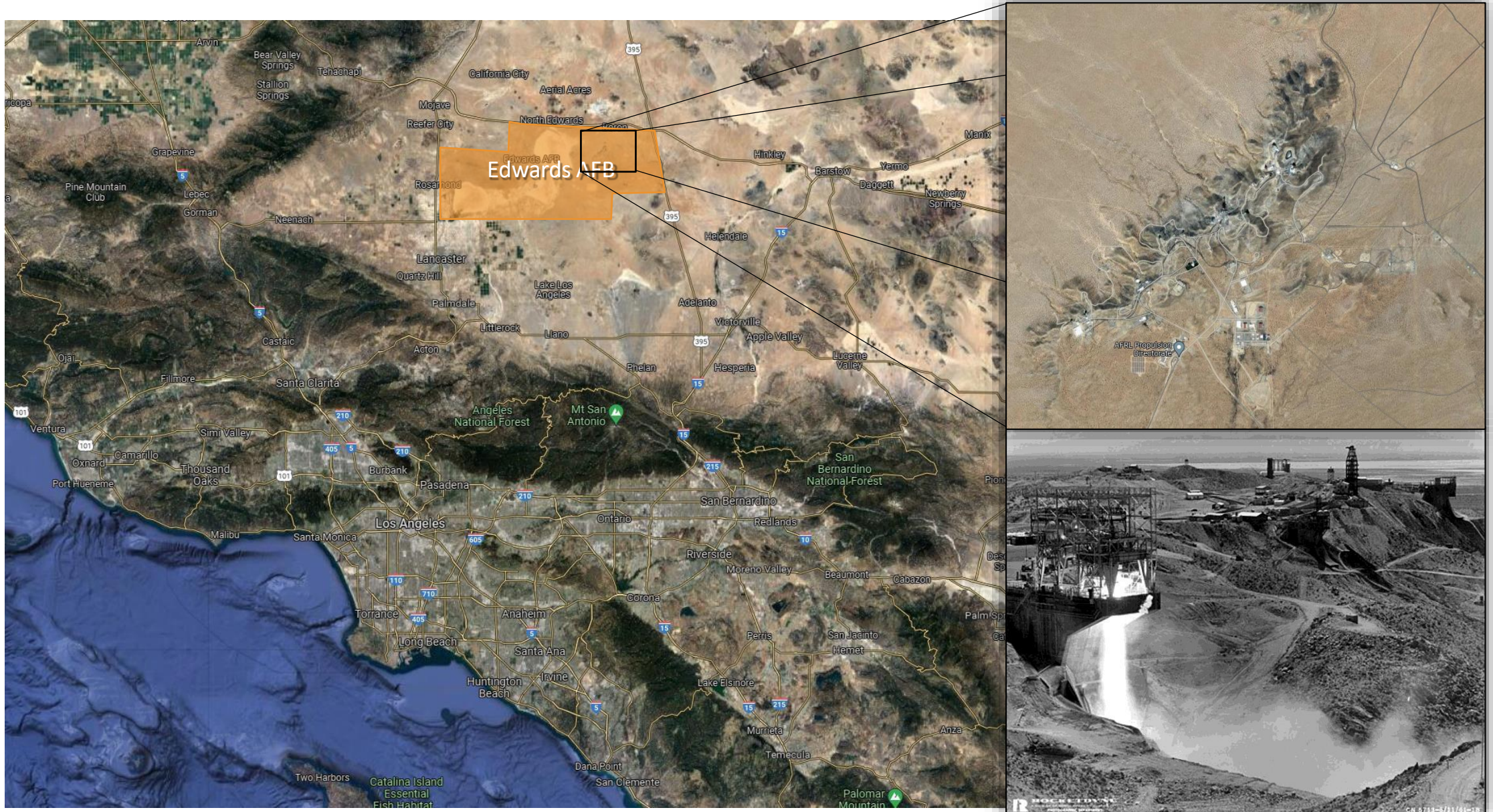


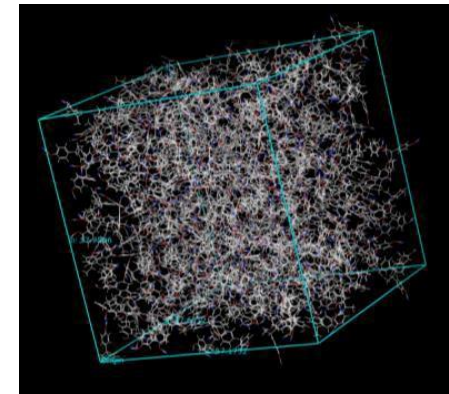
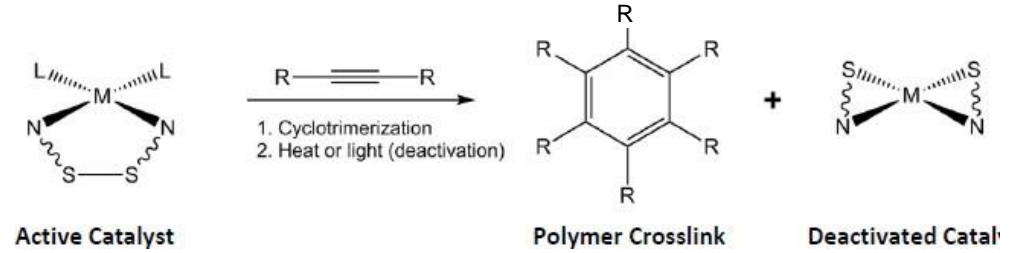
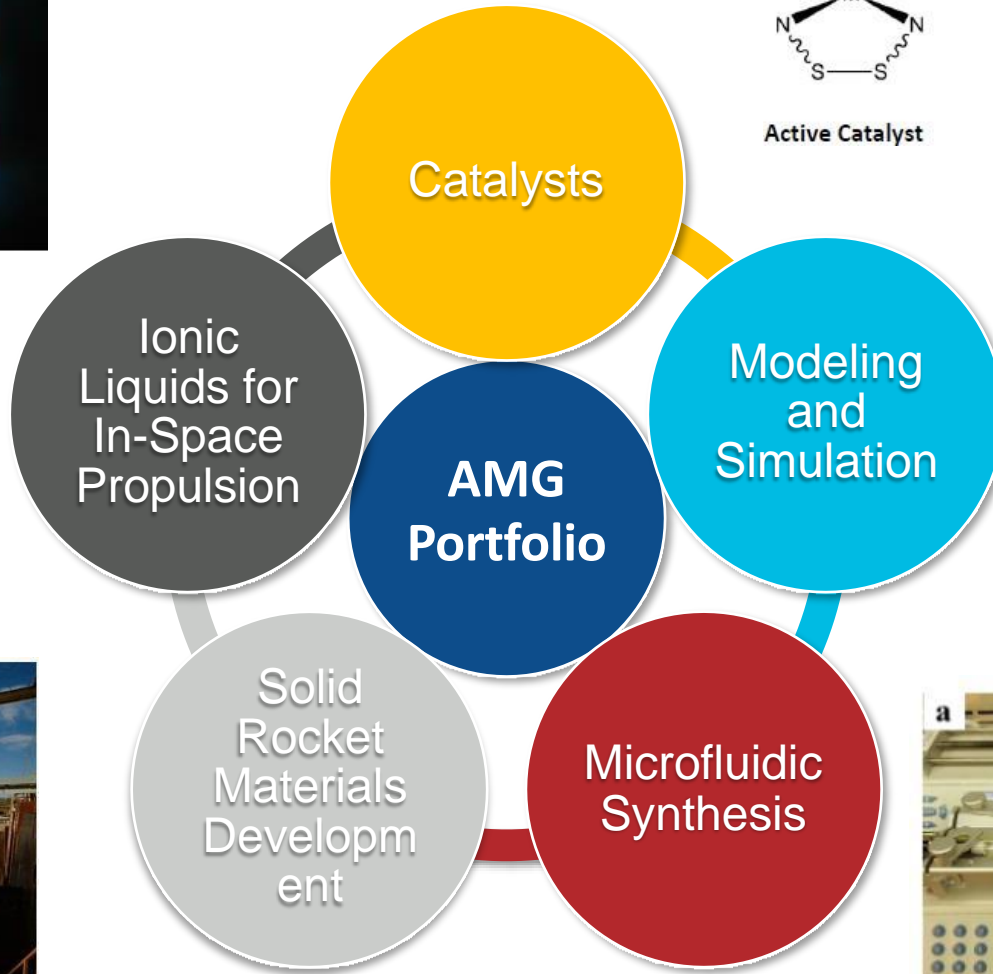
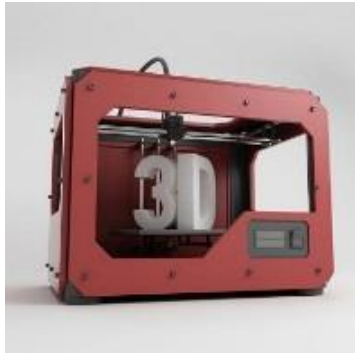
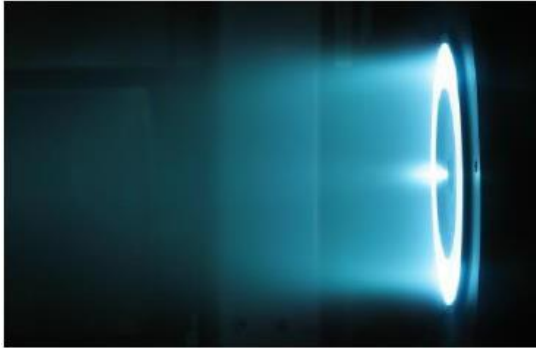
AFRL

Fluoropolymers for Propellant Binders: Towards Energy-Dense Polymers for Solid Rocket Motors

Alexander Lonnecker, PhD; Kamran Ghiassi, PhD

RQRP/AFRL 20 September 2021





Mission: to research and develop new materials for aerospace propulsion applications

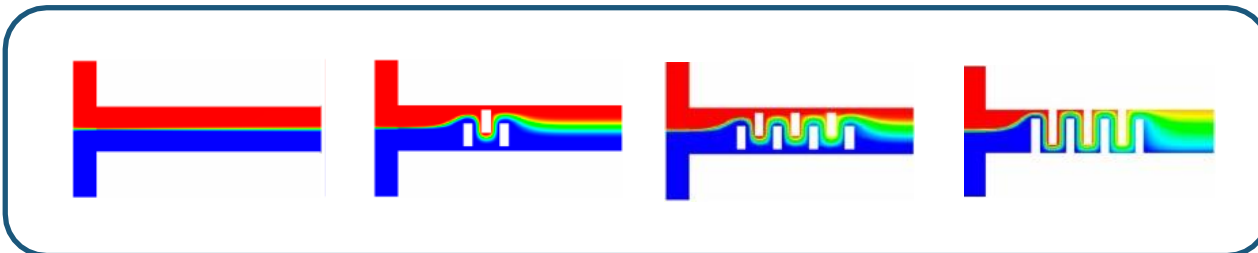
Advantages of Microfluidic Reactors

• Microfluidic Reactor Characteristics

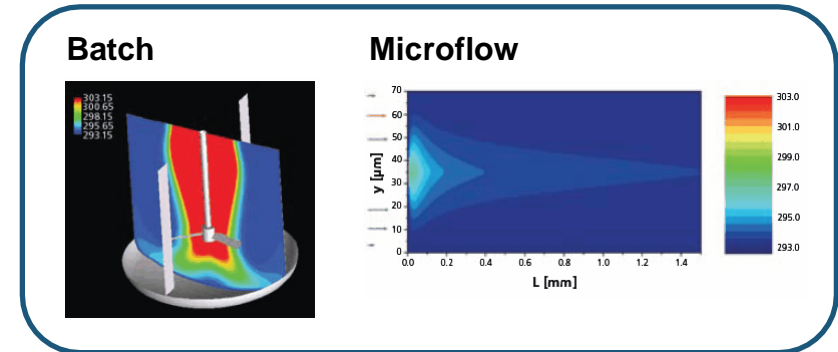
- Characteristic dimension < 1000 μm
- Reaction volume typically < 1 mL

Reactor Type	Surface Area / Volume (cm^2/cm^3)
Microreactor Channel (100 μm width)	200
100 mL Flask	1
50 Gallon Reactor	0.08
1000 Liter Reactor	0.06

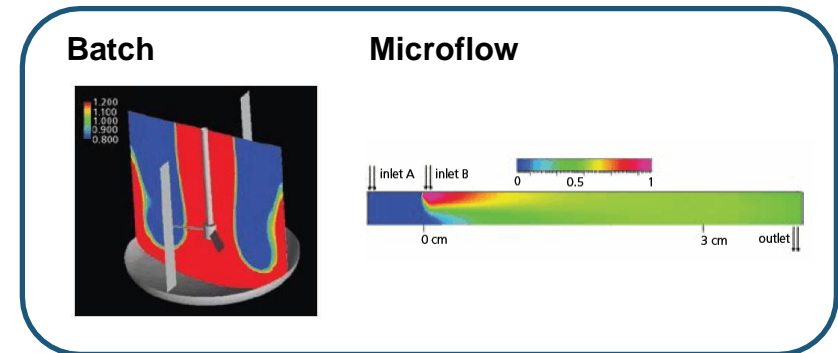
• Reactor Design



• Efficient Heat Transfer



• Efficient Mixing



- Unique properties driven by high SA / V
 - Better heat transfer, mixing

<https://www.sigmaaldrich.com/technical-documents/articles/chemfiles/microreactor-technology.html>



Advantages

- Fast reaction time
- Excellent temperature control
- Low reaction volume (safety, environmental)
- Scalability

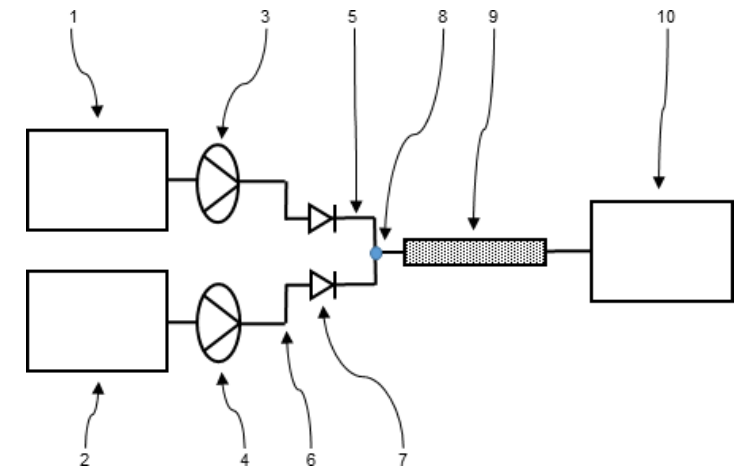
Technical Challenges

- Difficulty with heterogeneous systems (solid particles cause plugging)
- Up-front analytical development required (high throughput, detection of intermediates)

As a Tool for Polymer Development

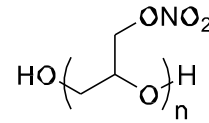
- Bridge the technological “valley of death” gap from bench top to demonstration article
- Potential control over degree of monomer functionality not possible in batch
- Good batch-to-batch reproducibility

- Microfluidic synthesis of phthalonitrile monomers: *patent pending*
- Microfluidic synthesis of cyanate ester monomers: *patent pending*
- Microfluidic anionic polymerization of butadiene: *patent in review*

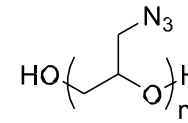




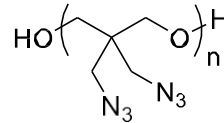
Energetic Polymers



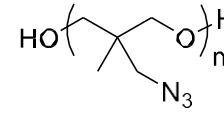
PGN



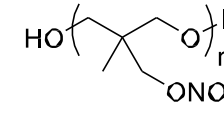
GAP



PBAMO



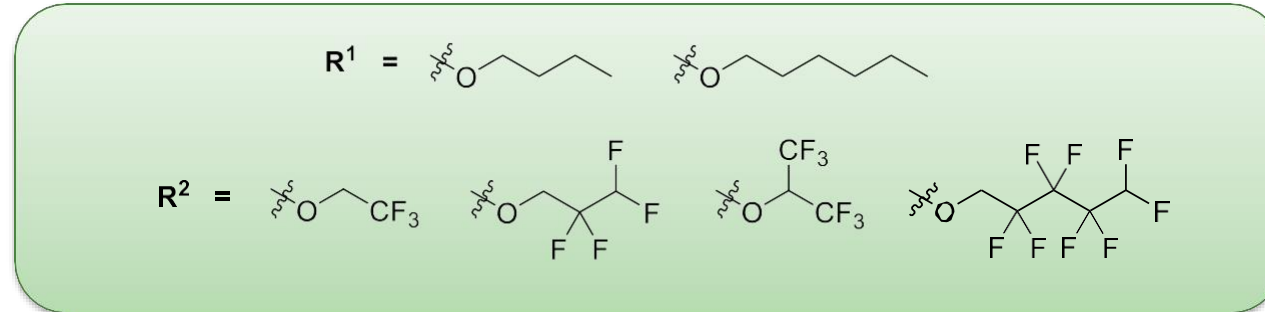
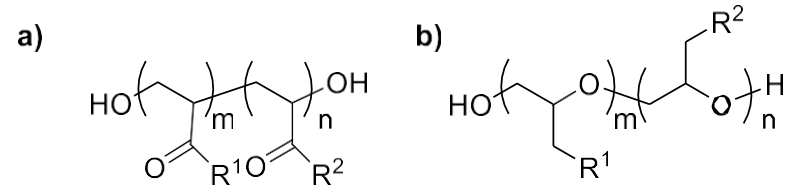
PAMMO



PNIMMO

- Synthesis of energetic binders primarily focuses on the incorporation of N-bearing moieties (azide, nitro, fluoroamine, etc)
- Issues associated with these polymers:
 - Higher T_g s,
 - Increased crystallinity
 - Lower thermal stabilities and higher shock/electrostatic sensitivity
- Strong demand for higher performing propellants remains
 - 5% increase in I_{sp} can increase ICBM range by 45%
 - FY21 JEMTP MATG1: “very high burning rate propellant formulations safe to manufacture at industrial scales”

Cheng, T. *Designed Monomers and Polymers*. 2019, 22, 54-65.



Increased energy output

- Fluorinated polymers react exothermically with electropositive metals such as magnesium and aluminum
 - Teflon/Viton/Mg compositions create more exothermic reactions (9.4 kJ/g) than TNT (3.72 kJ/g) and RDX (6.569 kJ/g)
- PTFE and Al generates 21 GJ/m³ (CL-20 and octanitrocubane <12 GJ/m³)

$$2Al + 3(-CF_2-)_n \rightarrow 3C + 2AlF_3, \Delta H^0 = -591.98 \text{ kJ}$$
- Investigated for infrared decoys, ignitors, flares, solid fuel rocket propellant, and explosive binder systems

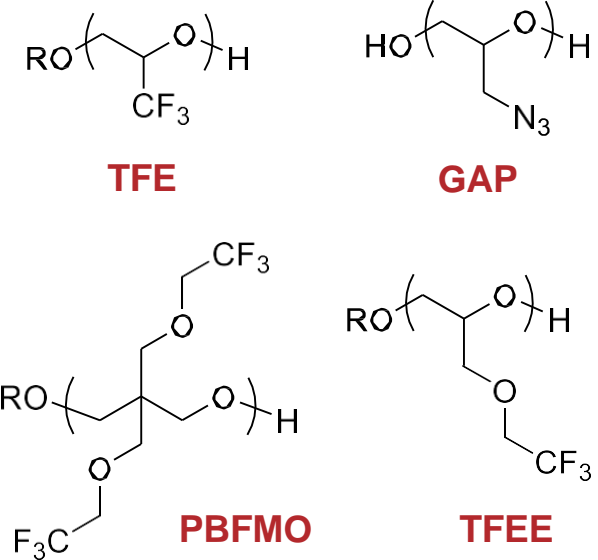
Rider, K.B.; et al. *Propellants Explos, Pyrotech.* **2013**, *38*, 433-440.

Yang, Y.; et al. *Appl. Phys. Lett.* **2004**, *9*, 1493-1495.

Improved mechanical and physical properties

Enhanced mechanical and physical properties

- Advantageous physiochemical properties over nitrogen containing polymers
 - High densities (GAP: 1.3 g/mL, PTFE ~2.1 g/mL, Viton/PVDF ~ 1.8 g/mL)
 - Long-term chemical stability
 - Good compatibilities with propellant ingredients (oxidizers, metal fuels, plasticizers, etc)
 - Thermal and impact stability
- Improved physical and mechanical properties and over azide containing polymers



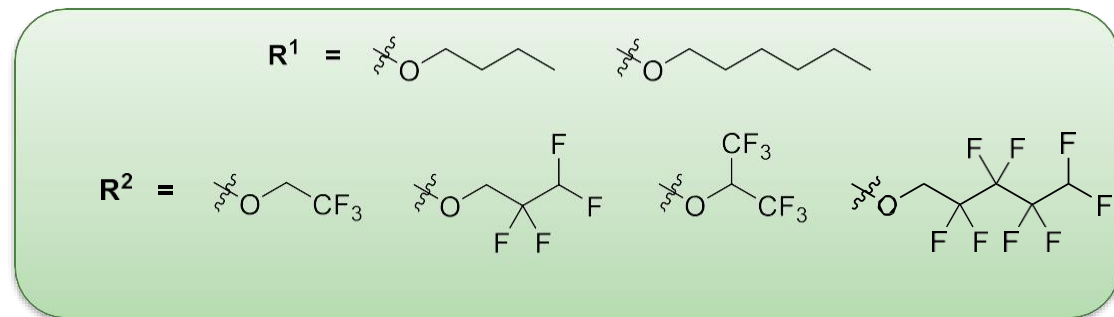
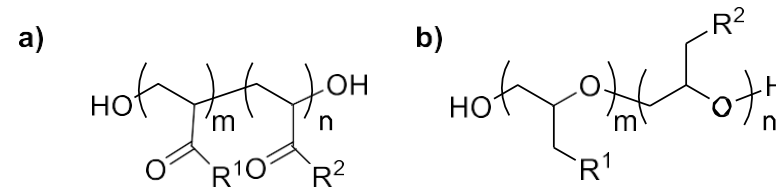
	Density (g/cm ³)	Viscosity at 25 °C (Pa·s)	H ₅₀ (cm)	T _g (°C)	Elongation at break (%)	Tensile Strength (MPa)
GAP	1.28	11.9	42.2	-45.1	101	2.4
TFEE/GAP	1.36	2.66	>129	-49.5	162.8	5.52

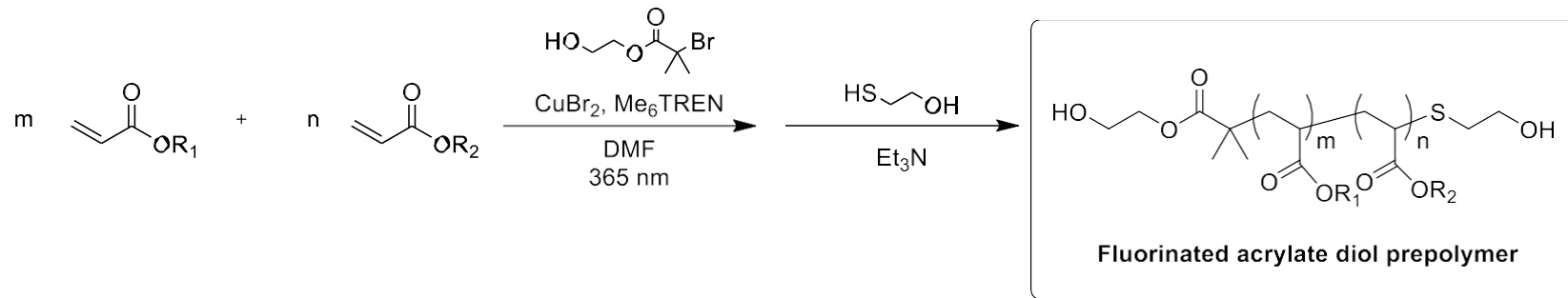
- More heat generated during cook-off tests with TFEE/GAP Al composites than with GAP homopolymer

Xu, M.; et al. *Polymers*. **2021**, *13*, 2706.
 Xu, M.; et al. *RSC Adv.*, **2017**, *7*, 47271-47278.
 Xu, M.; et al. *Polym Int.*, **2017**, *66*, 1318-1323.

Target goals for polymer binder

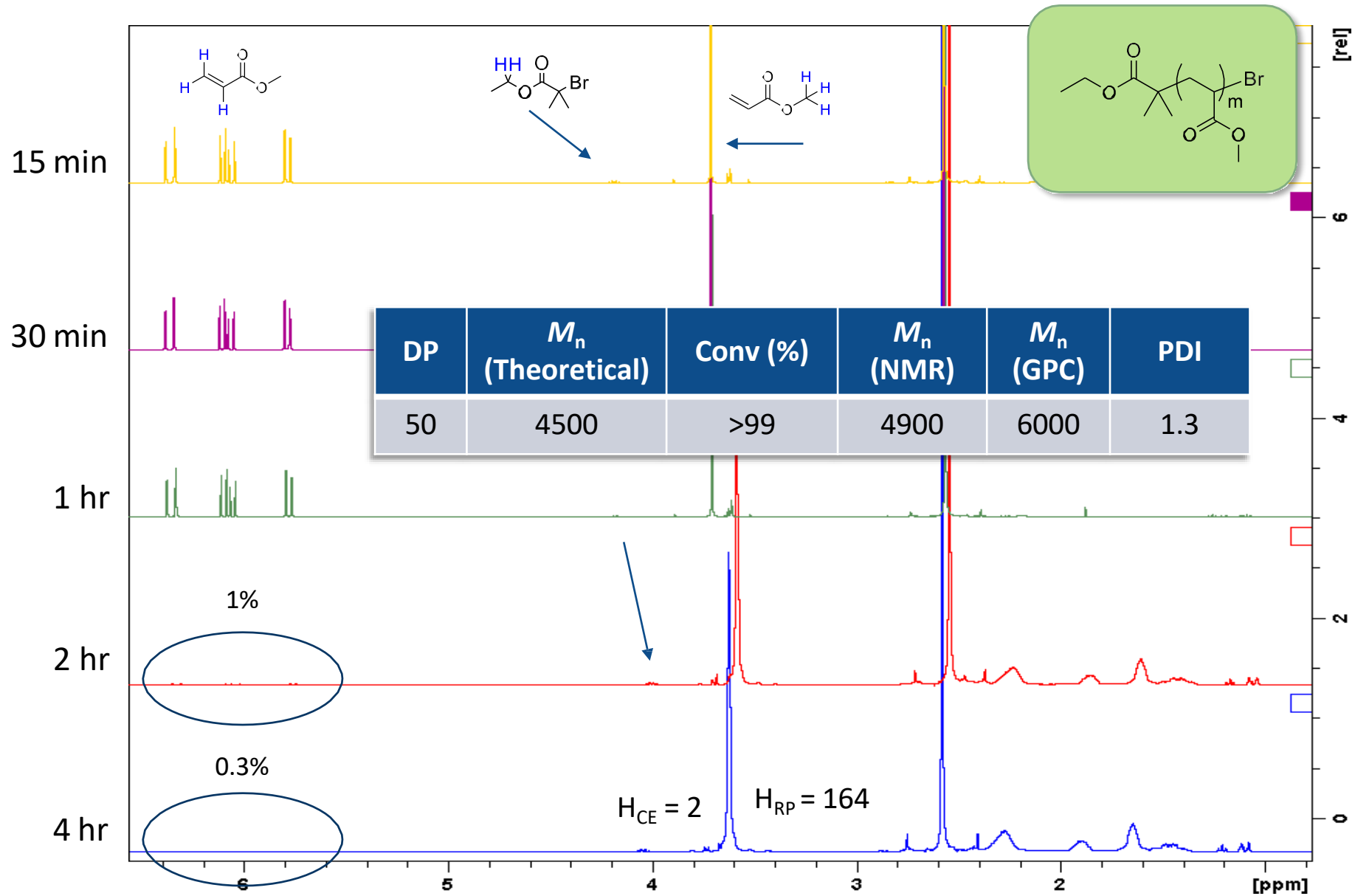
- Low PDI polymer with well-defined chain ends for crosslinking
- Low glass transition temperature (under -40 °C)
- Low melt viscosity
- Should retain mechanical integrity when filled with solids up to 80%
- Compatible with other ingredients of the composition
- High thermal stability
- Low sensitivity towards mechanical stimuli
- Easy handling and processing

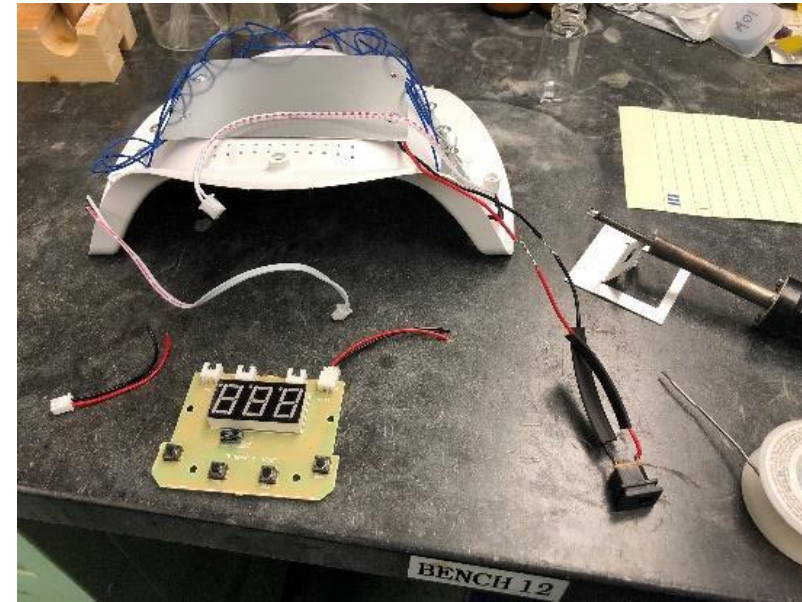
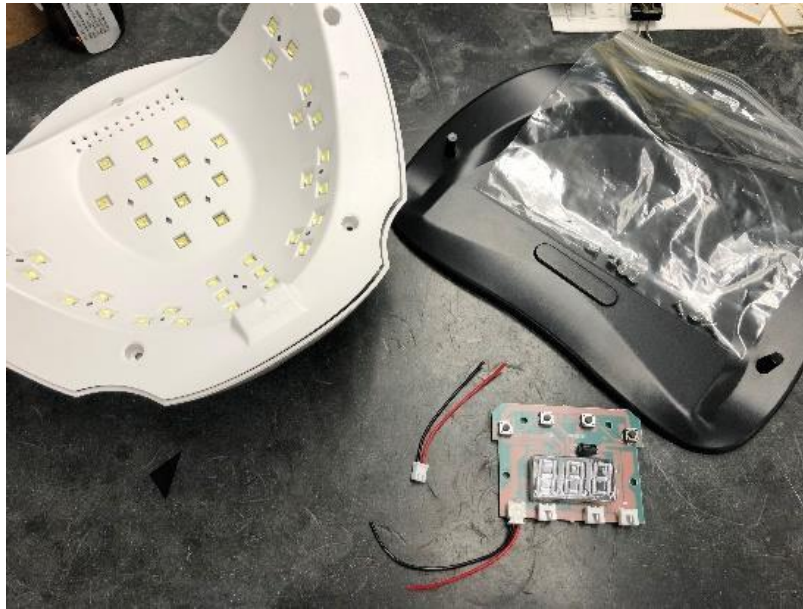




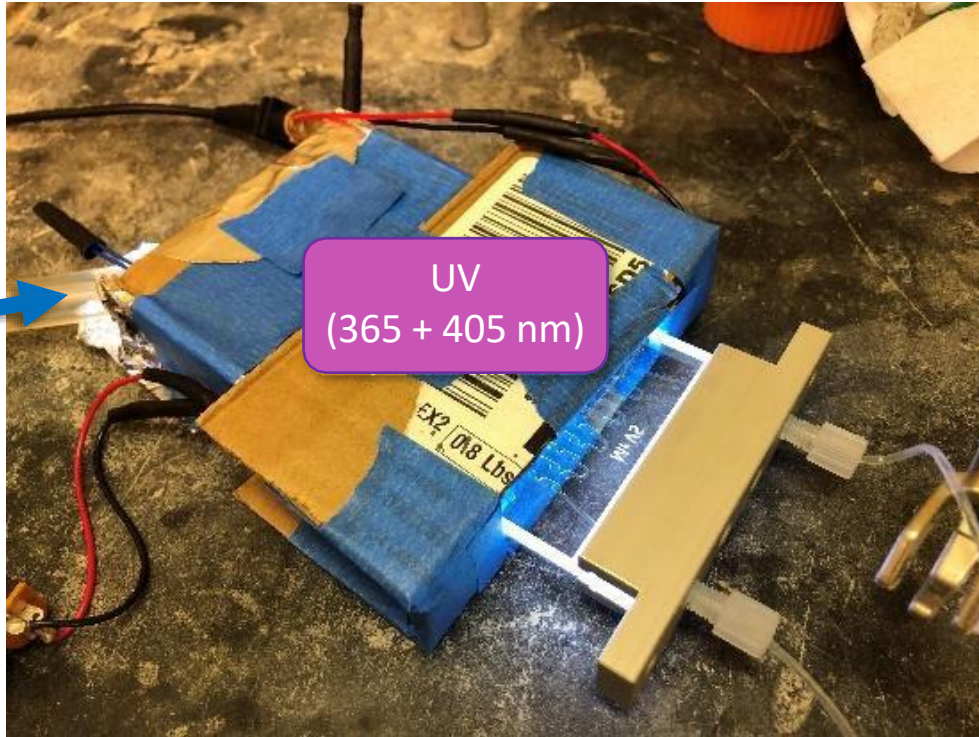
- Controlled radical polymerizations (RAFT/ATRP) enable the synthesis of well-defined acrylate polymers
 - Acrylate system: relatively low T_g and easily modifiable side arms
 - Low PDI
 - Chain end chemistry critical for crosslinking
- Efficient photoATRP conditions
 - Oxygen insensitive
 - Relatively fast ATRP conditions
- Application of microfluidics
 - More efficient photoreactors may lead to faster reaction times
 - More reliable scale up

Ultra-low volume oxygen tolerant photoinduced Cu-RDRP. *Polym Chem.* **2019**, *10*, 923-971.





- LED light source
 - Affordable off the shelf nail dryer (about \$25)
 - 80 W LED lights
 - Timer switches bypassed for light to run continuously
- LED light source in batch and flow led to faster reaction rates with methyl acrylate (under 1 hour in flow)

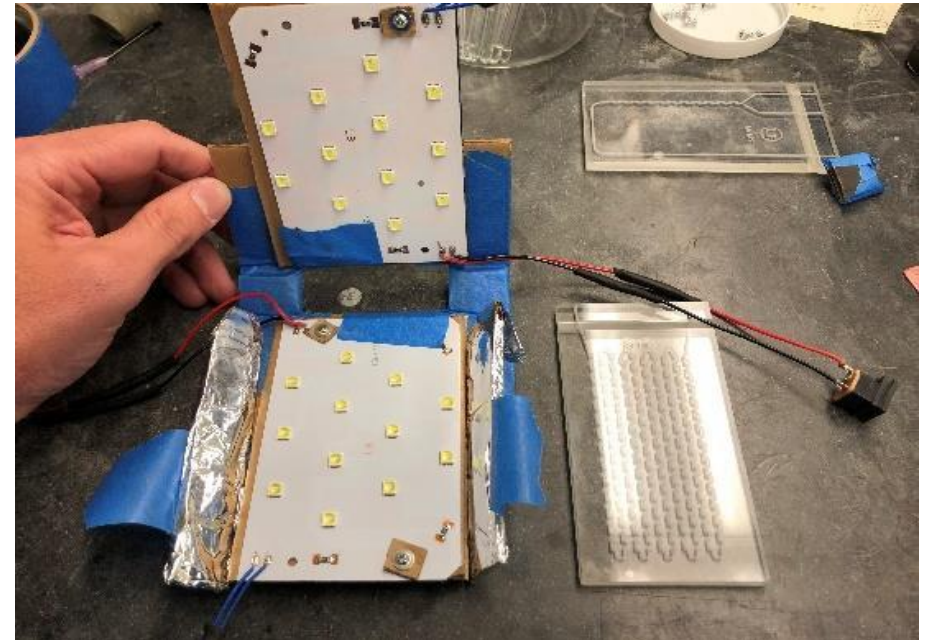
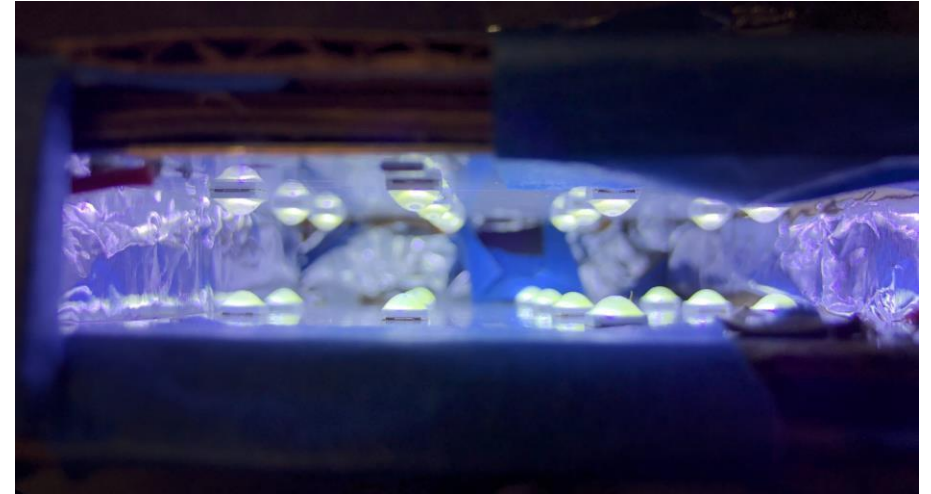


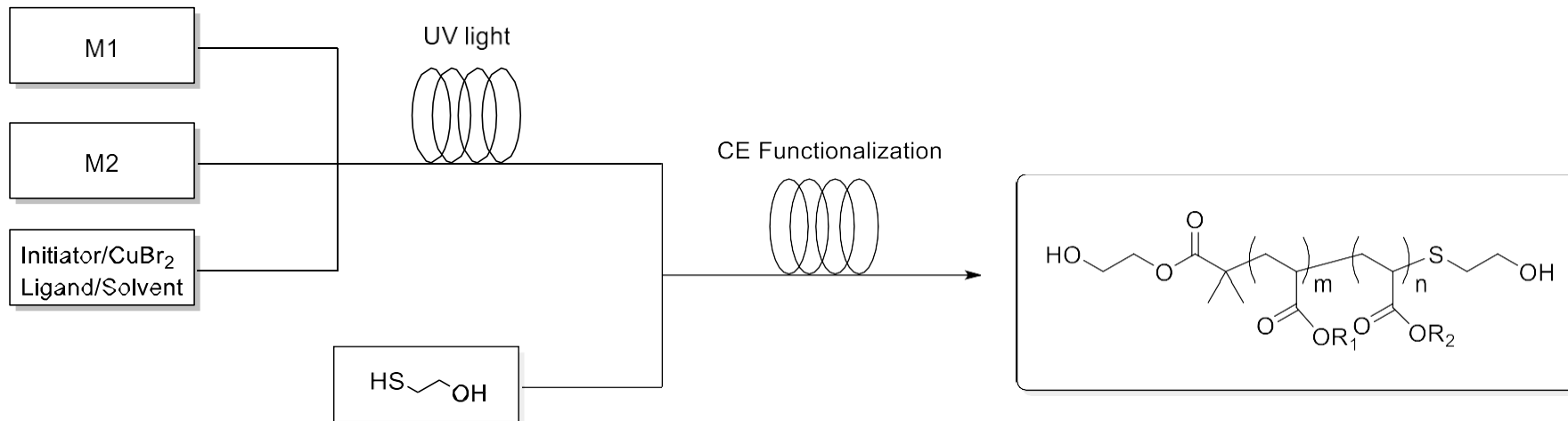
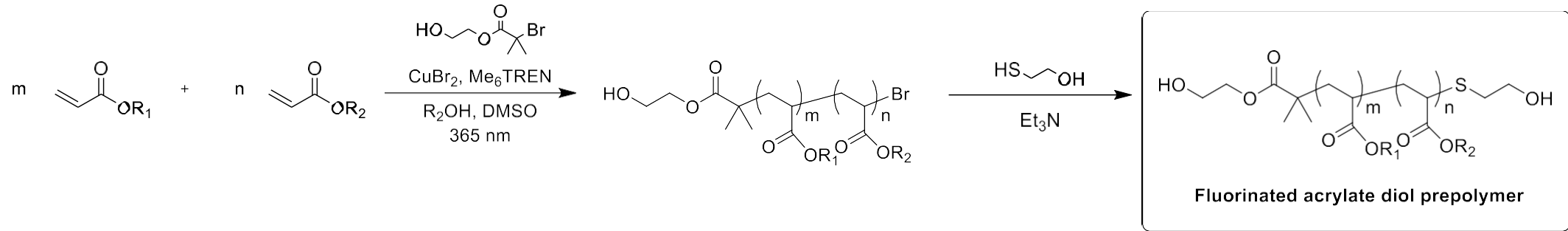
N₂
(cooling)

UV
(365 + 405 nm)

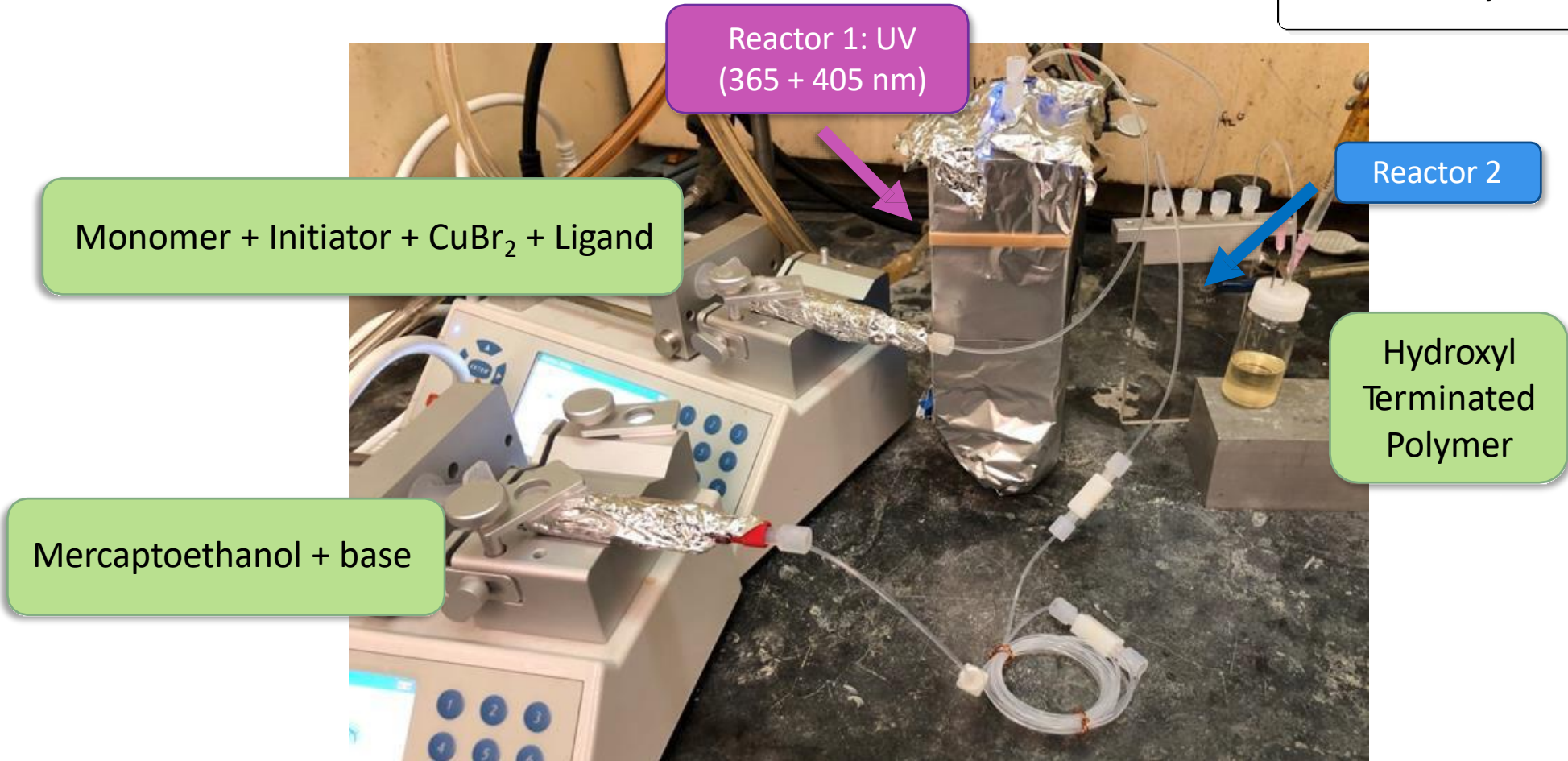
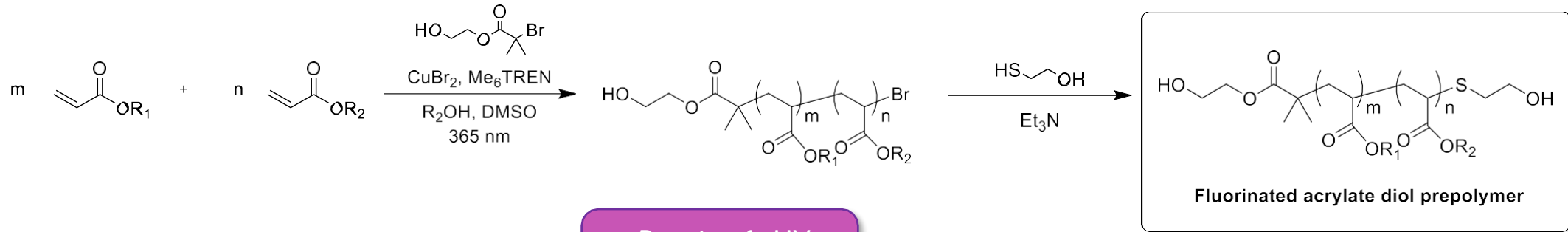
Syringe Pump
Monomer + Initiator
CuBr₂ + Ligand

Polymer

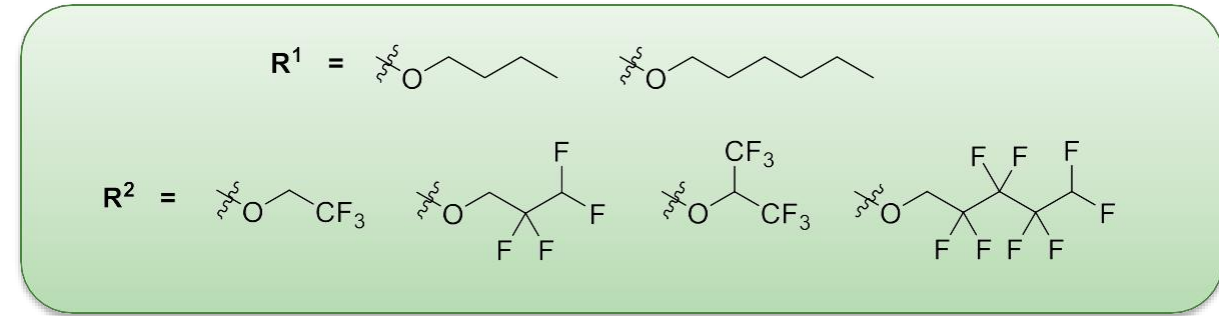
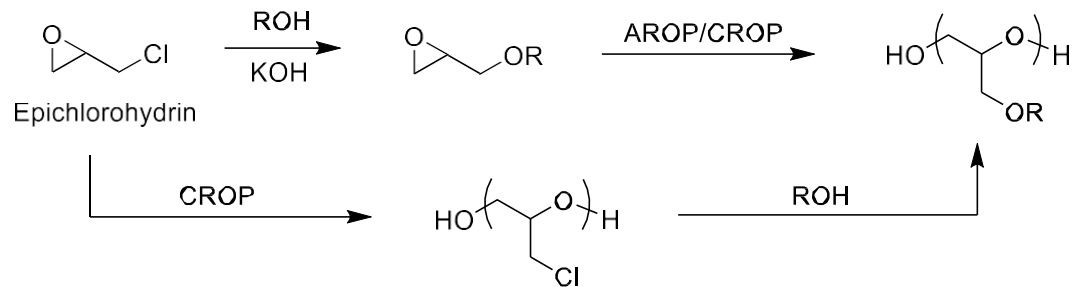




- Two step process for the production of acrylate-based fluorinated diol prepolymers
- Photo induced ATRP allows for good control (PDI <1.1) and quick copolymerizations (30-150 min for 95+% conv)
- Thio-bromo click reaction allows for the installation of OH chain ends with mercaptoethanol
- Both reactions tested in flow and performed in tandem



Possible Synthetic routes for Fluorinated Polyethers



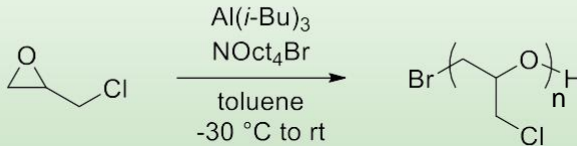
Anionic ring opening (AROP)

- Controlled polymerization (linear conversion, low PDI)
- Requires high temperature (>60 °C)
- Limit to achievable M_w
- Not compatible with ECH, must functionalize before polymerization

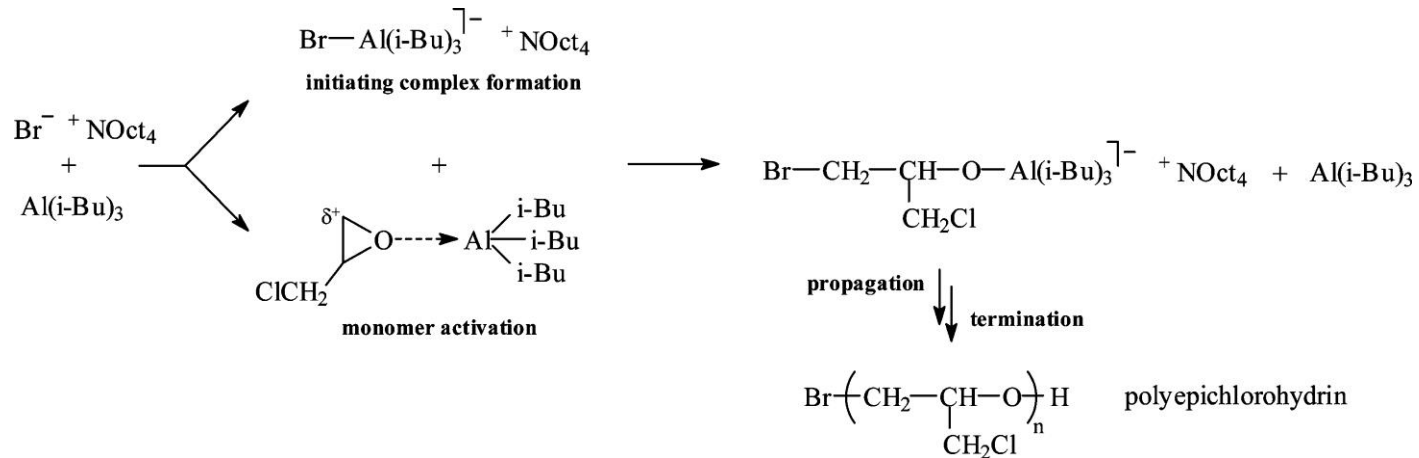
Cationic Ring Opening (CROP)

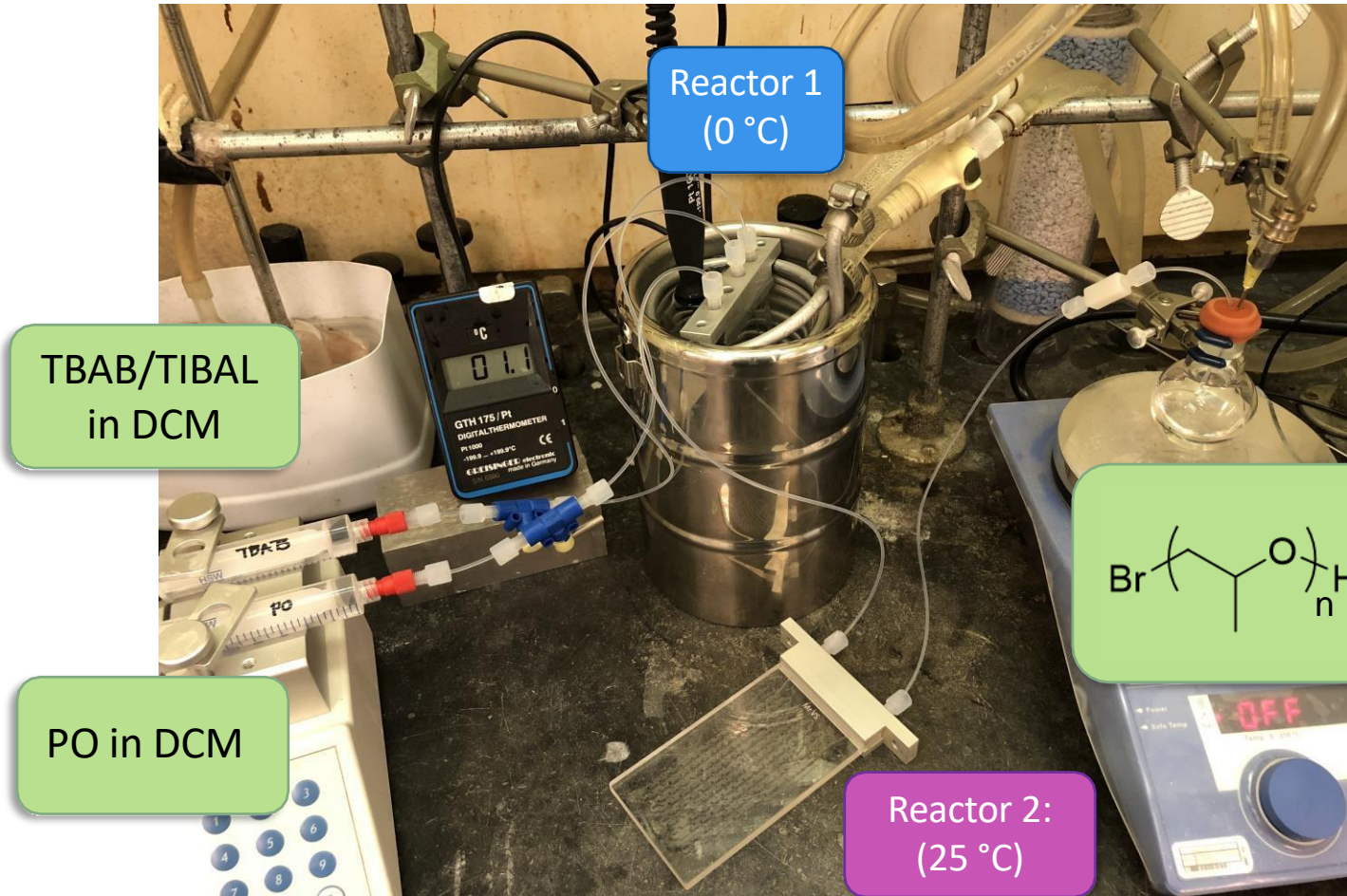
- ECH compatible
- Requires specific conditions to achieve low PDIs
- Very long reaction times needed for full conversion

MAROP of Epichlorohydrin

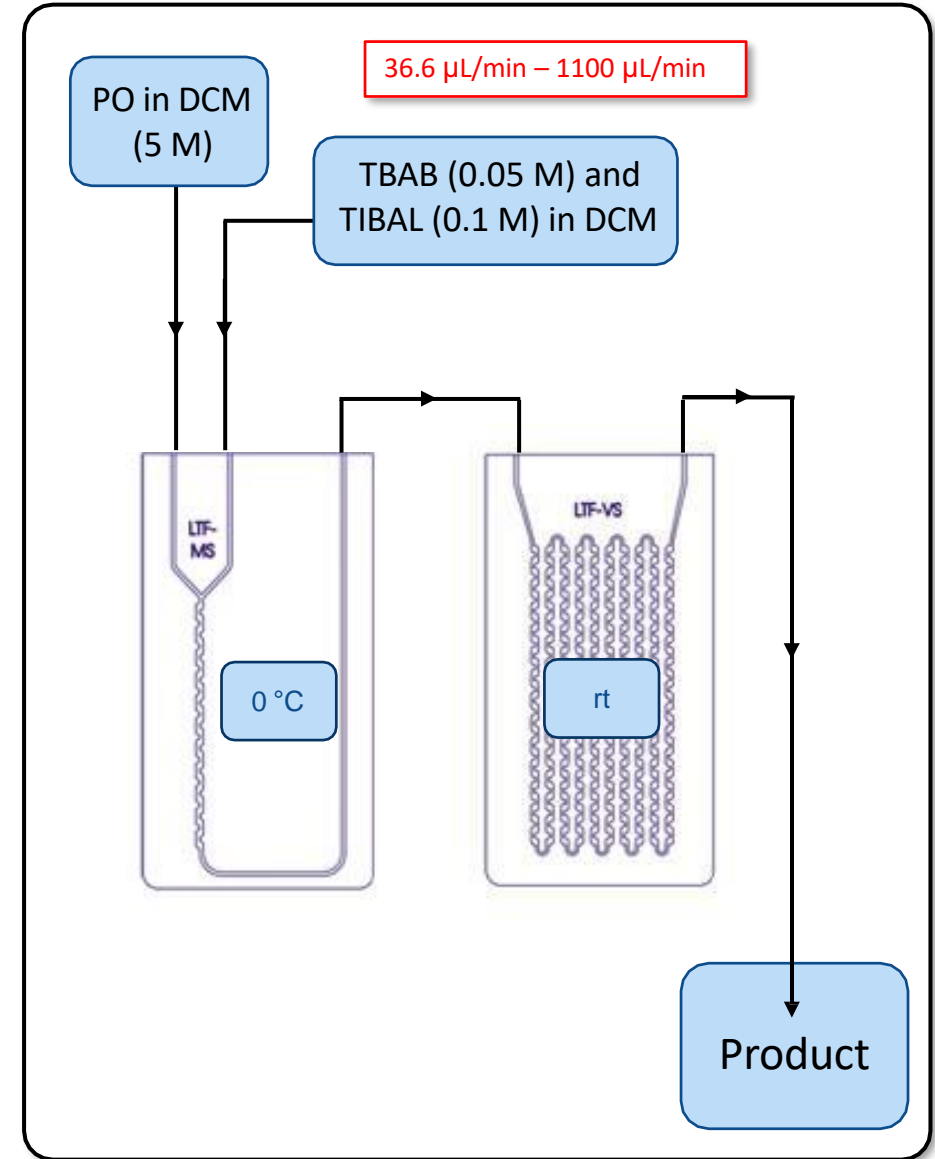


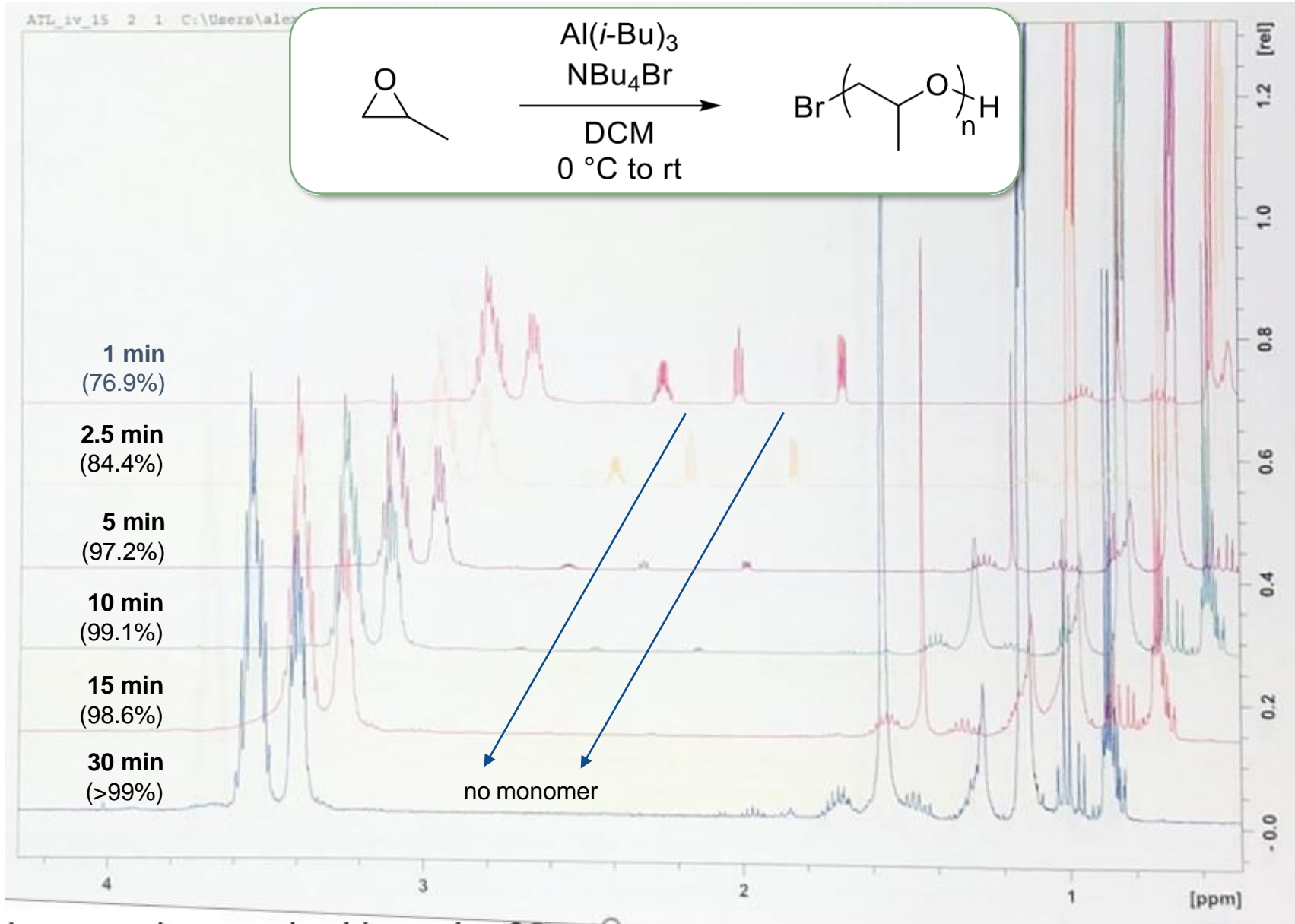
Stéphane Carlotti, Amélie Labbé, Virginie Rejsek, Stéphane Doutaz, Matthieu Gervais, and Alain Deffieux
Macromolecules. **2008**, *41*, (19), 7058-7062

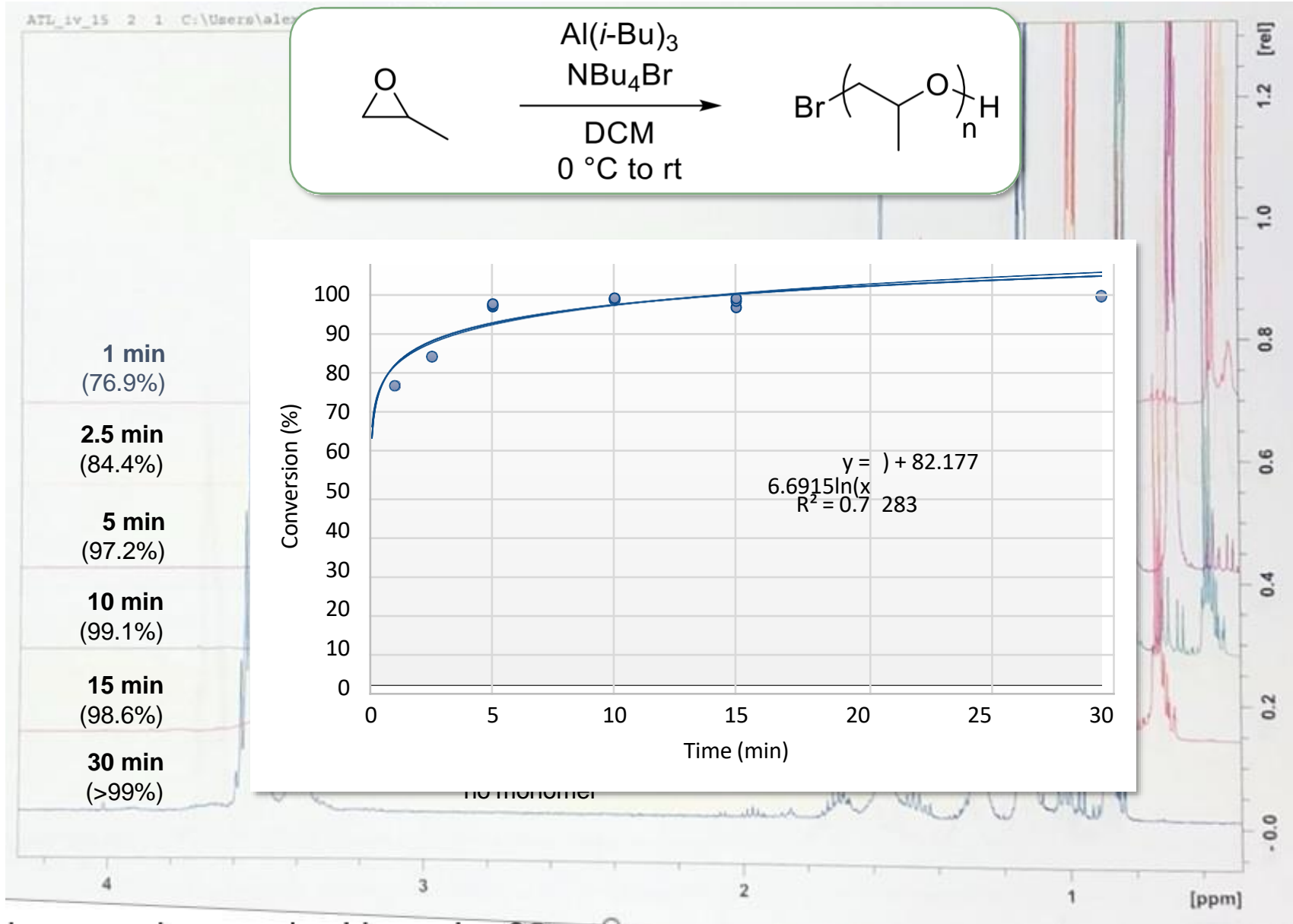




- Two stage reaction at 0 °C and room temperature
- Conversion measured as flow rate/retention time varied
- Full conversion reached in under 30 min



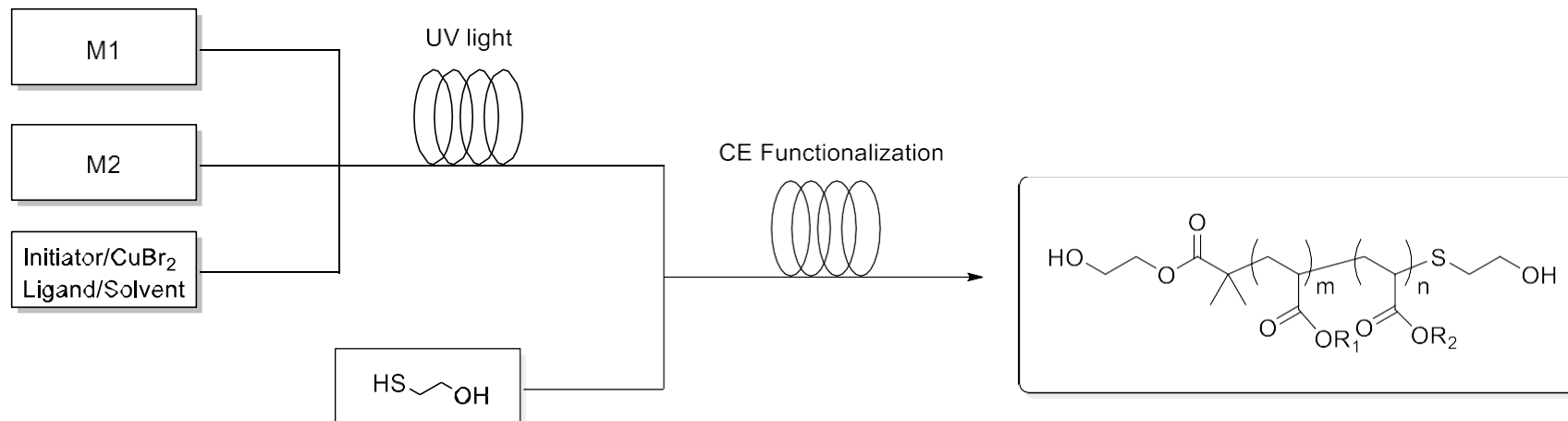




Overview and Future Outlook

Fluoroacrylate polymers

- Identified appropriate solvent/ligand for all butyl and trifluoroethyl monomers
- Increased photo-efficiency with glass microreactor
- Further optimize ω -chain end modification
- Synthesize and assess fluorinated copolymers for scale-up

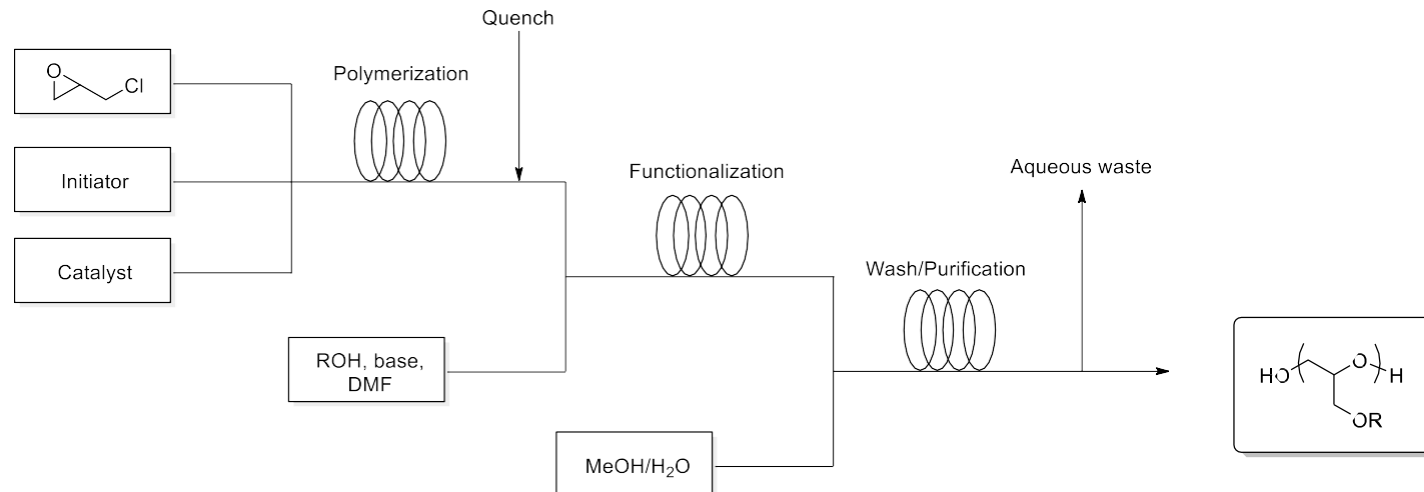




Overview and Future Outlook

Polyether fluoropolymers

- Ultrafast polymerization of PO in microflow using MAROP conditions
- Thio-bromo chain end modification successful without the need of additional base
- Apply conditions to other appropriate monomers (ECH, etc)
- Establish reaction conditions for the installation of side arms on PECH
- Synthesize and assess fluorinated polyether copolymers





Questions?



Overview and Future Outlook

Polyether fluoropolymers

- Ultrafast polymerization of PO in microflow using MAROP conditions
- Thio-bromo chain end modification successful without the need of additional base
- Apply conditions to other appropriate monomers (ECH, etc)
- Establish reaction conditions for the installation of side arms on PECH
- Synthesize and assess fluorinated polyether copolymers

