

# Designing Next Generation Polymer- Based Surfactants for Fire Suppression (WP-1559)

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COLLEGE OF SCIENCE  
**CHEMISTRY**  
VIRGINIA TECH.



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Advancing the Science of Safety



Arizona State  
University

## Objectives

1. Design a polymeric surfactant platform of **all-aromatic, polyimides**
2. Demonstrate **crosslinkable** all-aromatic **aqueous** polyimide foams
3. Explore versatile pendant **sulfonates** to further tailor fire performance



*Foamed formulation*

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# REPORT DOCUMENTATION PAGE

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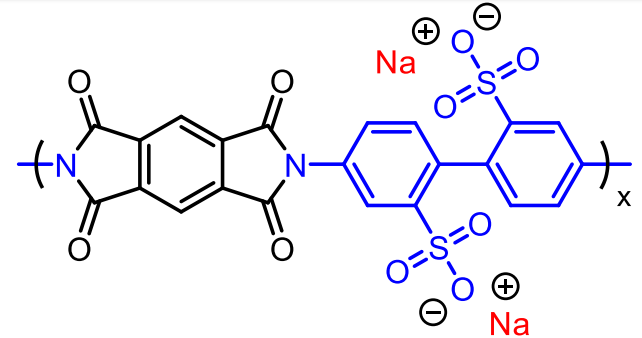
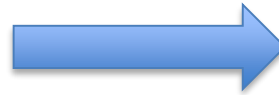
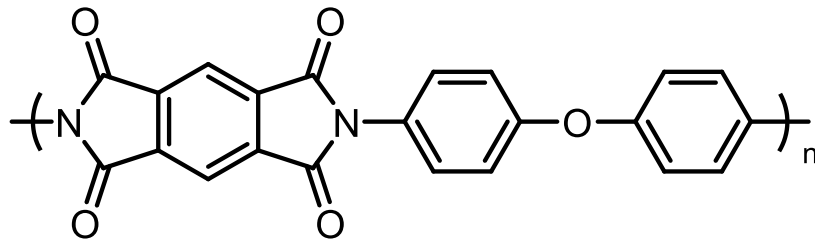
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<b>1. REPORT DATE (DD-MM-YYYY)</b> 11/12/2020		<b>2. REPORT TYPE</b> SERDP Project Outbrief		<b>3. DATES COVERED (From - To)</b> 1/3/2019 - 1/3/2021	
<b>4. TITLE AND SUBTITLE</b> Designing Next Generation Polymer Based Surfactants for Fire Suppression				<b>5a. CONTRACT NUMBER</b> 19-P-0001	
				<b>5b. GRANT NUMBER</b>	
				<b>5c. PROGRAM ELEMENT NUMBER</b>	
<b>6. AUTHOR(S)</b> Dr. Timothy E. Long, Benjamin J. Stovall, Clay B. Arrington Virginia Polytechnic Institute and State University  Joshua B. Dinaburg, Dr. Brian Y. Lattimer Jensen Hughes				<b>5d. PROJECT NUMBER</b> WP18-1559	
				<b>5e. TASK NUMBER</b>	
				<b>5f. WORK UNIT NUMBER</b>	
<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b> Virginia Polytechnic Institute and State University 1040 Drillfield Drive Davidson Hall, Rm 480 (0212) Blacksburg, VA 24061				<b>8. PERFORMING ORGANIZATION REPORT NUMBER</b> WP18-1559	
<b>9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b> Strategic Environmental Research and Development Program 4800 Mark Center Drive, Suite 16F16 Alexandria, VA 22350-3605				<b>10. SPONSOR/MONITOR'S ACRONYM(S)</b> SERDP	
				<b>11. SPONSOR/MONITOR'S REPORT NUMBER(S)</b> WP18-1559	
<b>12. DISTRIBUTION/AVAILABILITY STATEMENT</b> DISTRIBUTION STATEMENT A. Approved for public release: distribution unlimited.					
<b>13. SUPPLEMENTARY NOTES</b>					
<b>14. ABSTRACT</b> The technical objectives of this project are listed below: <ul style="list-style-type: none"> <li>• 1. Design a polymeric surfactant platform of all aromatic, polyimides</li> <li>2. Demonstrate crosslinkable all aromatic aqueous polyimide foam</li> <li>3. Explore versatile pendant sulfonates to further tailor fire performance</li> </ul>					
<b>15. SUBJECT TERMS</b> Polymer Based Surfactants, Fire Suppression, AFFF					
<b>16. SECURITY CLASSIFICATION OF:</b>			<b>17. LIMITATION OF ABSTRACT</b>  UNCLASS	<b>18. NUMBER OF PAGES</b>  26	<b>19a. NAME OF RESPONSIBLE PERSON</b> Timothy Long
<b>a. REPORT</b>  UNCLASS	<b>b. ABSTRACT</b>  UNCLASS	<b>c. THIS PAGE</b>  UNCLASS			<b>19b. TELEPHONE NUMBER (Include area code)</b> 540-231-2480





# Innovative polymer “solutions” to combat use of fluorosurfactants



## Aromatic polyimides display advantageous properties:

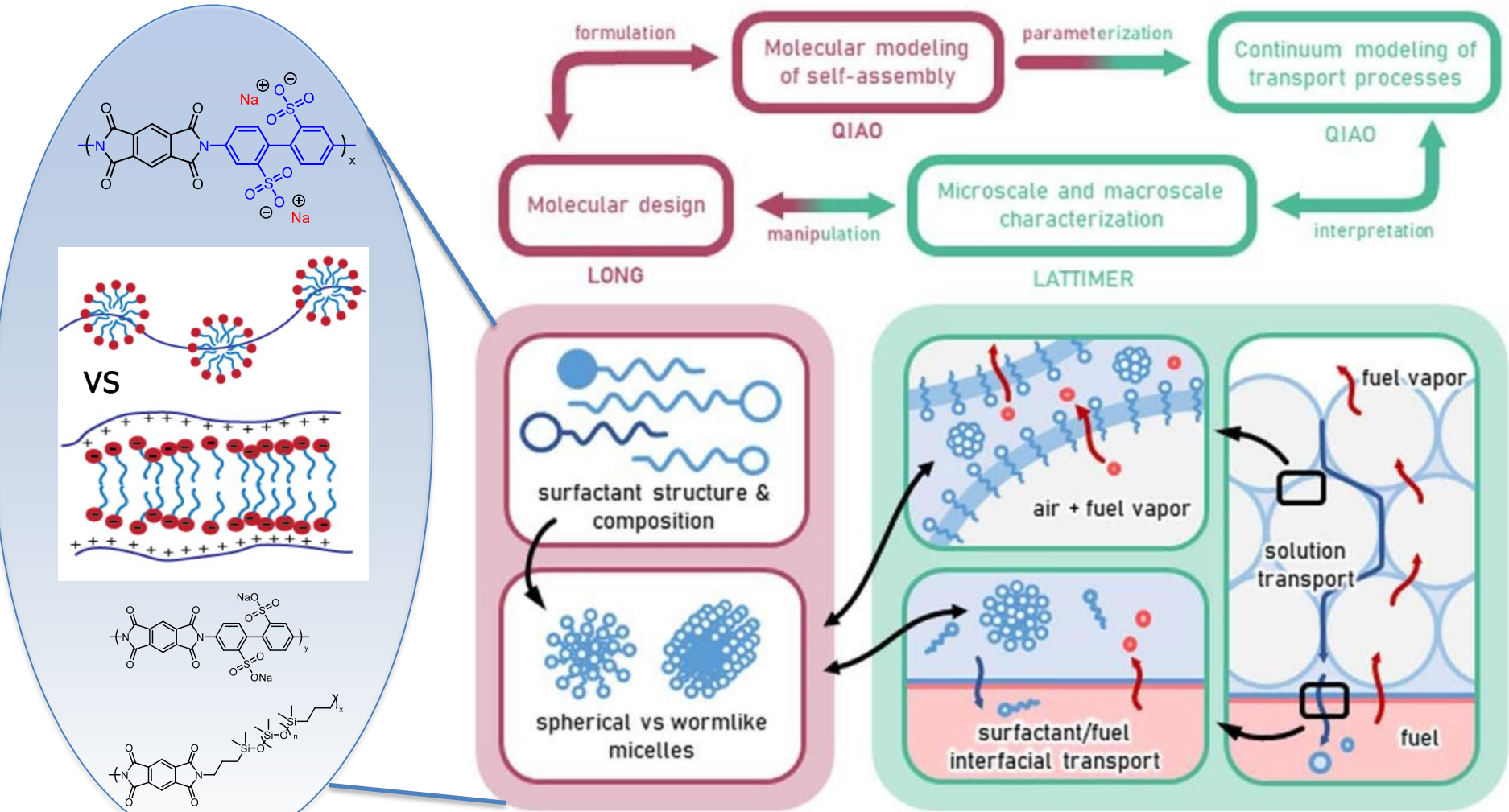
- Operating temp. up to 450 °C
- Elastic modulus 2+ GPa
- **High UL-94 flammability rating**
- Thermal, electrical, radiation resistance
- **Insoluble/non-dispersible in water**

## Sulfonated fully aromatic PI:

- ✓ **Water soluble/dispersible**
- ✓ **High char yields**
- ✓ **Surfactant miscibility**
- ✓ **Ionic/ compositional modularity**

Next generation fluorine-free foams based on a novel polymer technology, which meet fire qualification requirements, limit environmental impact, and are compatible with existing AFFF equipment

# Foam behavior can be investigated with regard to a modular molecular design

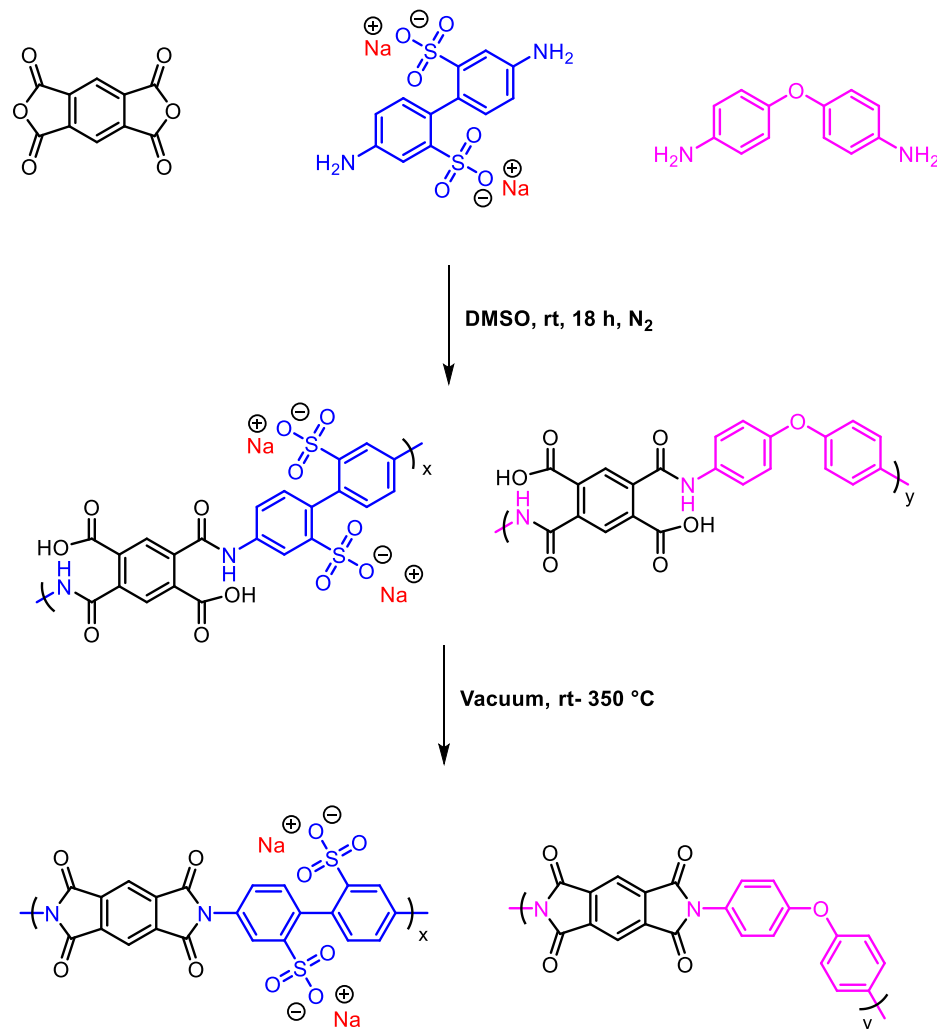


# Two-step polycondensation yields thermally stable sodiosulfonated polyimides

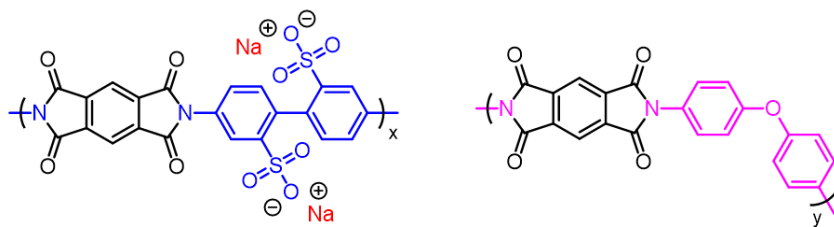
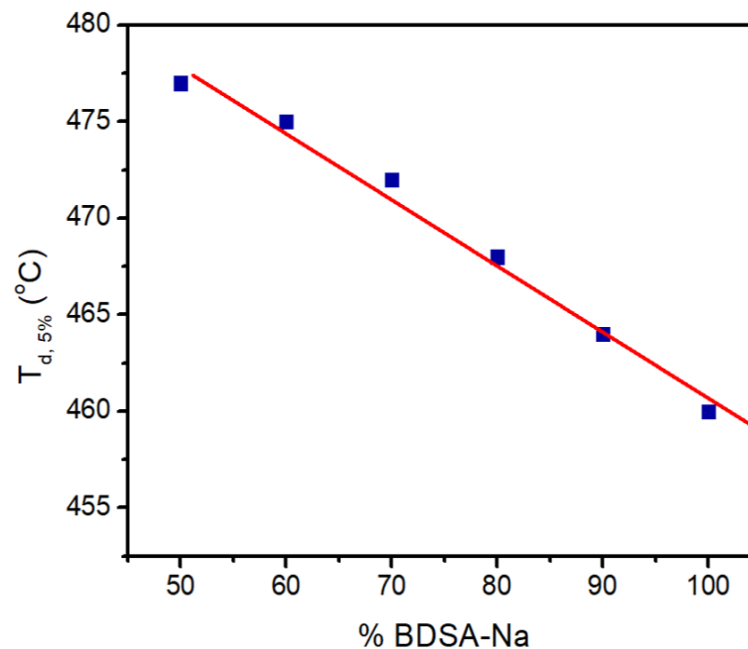
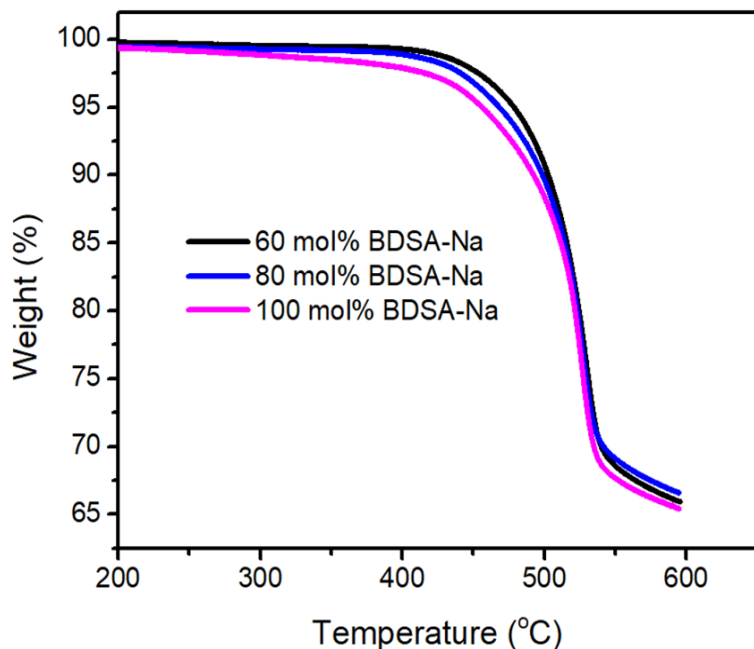
From pyromellitic dianhydride (**PMDA**), sodium salt of 4,4'-diamino diphenyl 2,2'-disulphonic acid (**BDSA-Na**) and 4,4'-oxydianiline (**ODA**)

➤ 100-50 mol% **BDSA-Na**: **ODA**

After imidization up to 400 °C, free-standing films, deep brown, with varying flexibility

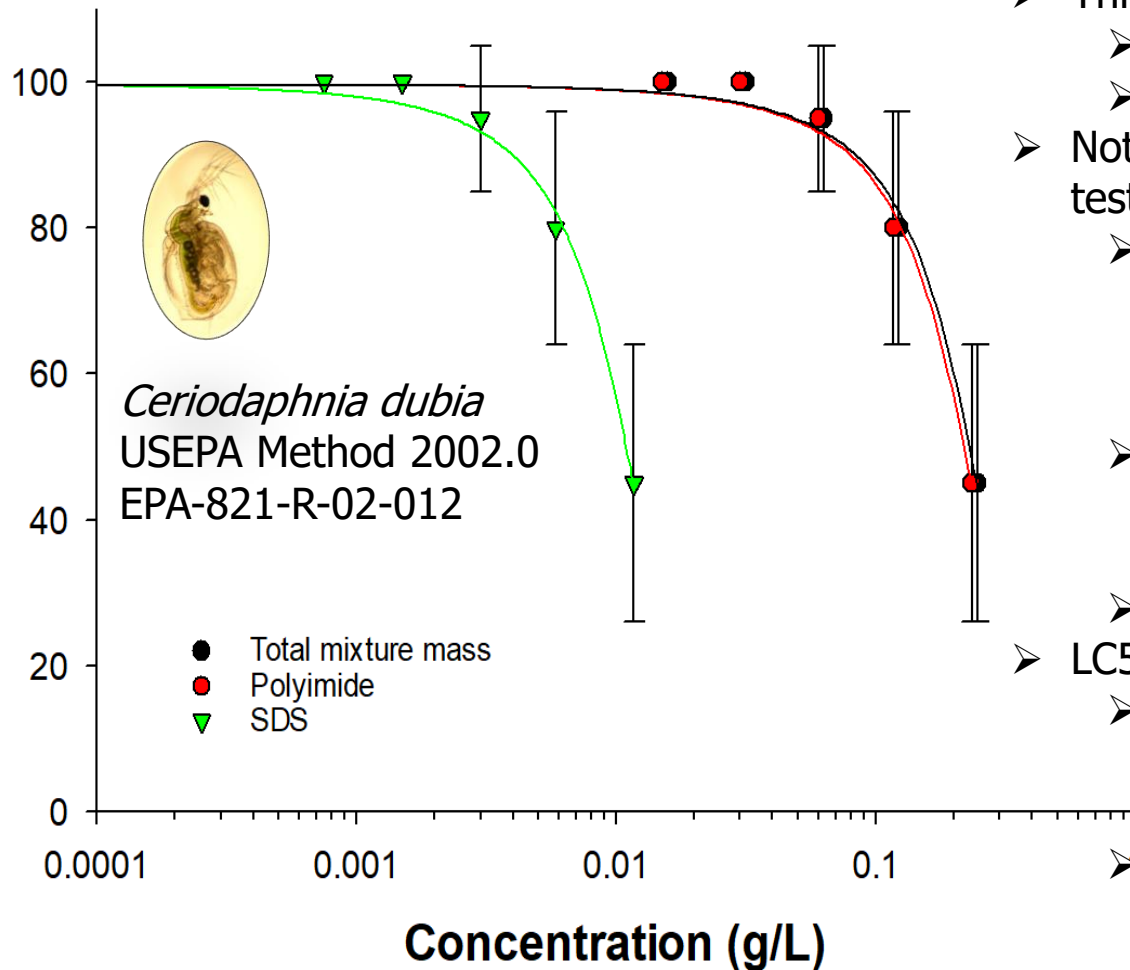


# Thermal characterization reveals high char yields and competitive weight loss temperatures



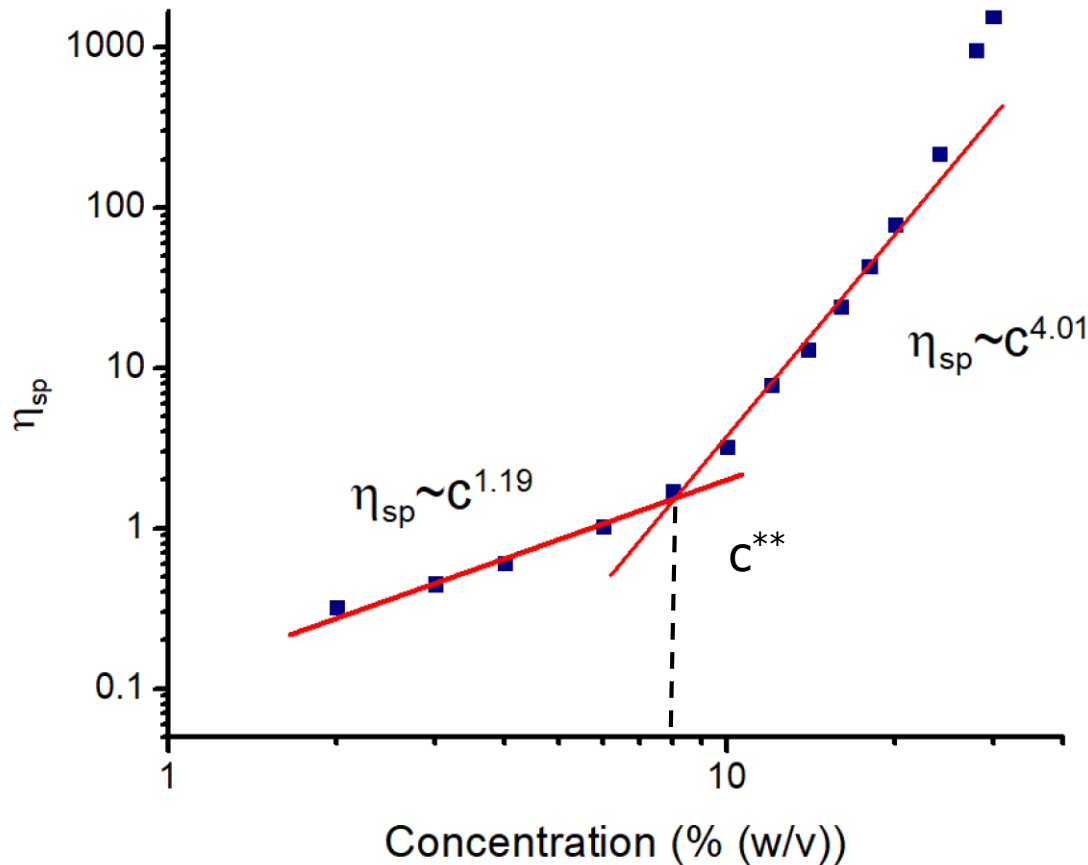
- $T_{d,5\%}$  remains the same under air, 60-70%
- Changes in char yields are negligible between different polymers

# Preliminary ecotoxicology provides insight into environmental effects



- This is a mixture
  - Cause for toxicity **uncertain**
  - Polyimide + SDS
- Note: only single 48-hour acute toxicity test conducted on the mixture
  - Concentrations expressed as individual constituents from the mixture (from one test) but there may be synergistic effects
  - **Individual constituent tests not conducted but are planned**
  - All concentrations nominal
- LC50 values (nominal)\*
  - Expressed in terms of polyimide
    - LC50 = **216 (162 – 430) mg/L\***
  - Expressed in terms of SDS
    - LC50 = **11 (8 – 21) mg/L\***

# Solution viscosity models and predicts solution behavior

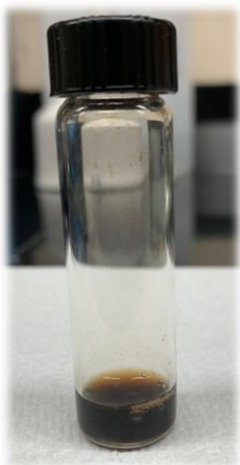
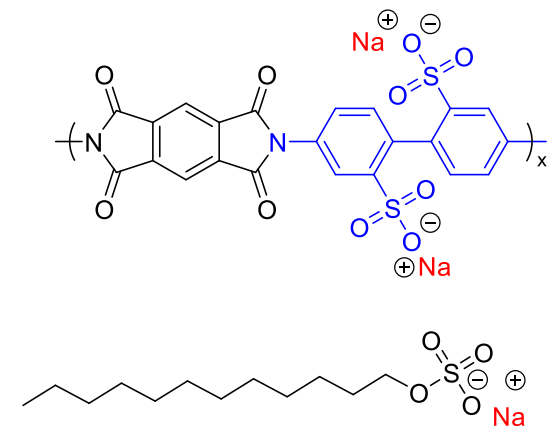


- $C^{**}$ , crossover into entanglement  $\sim 8$  wt.%
- Deviations at high concentrations due to lower molecular wt. polymer and dispersity
- Scaling theory indicates a polyelectrolyte solution with salt present!
  - Not quite at neutral limit
  - Being studied further

# Fully water soluble, foam-forming polyimides at high degrees of sulfonation

## PIs with 100 and 75 mol% **BDSA-Na**, fully water soluble

- Minimal foam-forming ability in unmodified polymer solution
- Addition sodium dodecyl sulfate (SDDS), produced stable foams after agitation



3 wt.% PI



0.12 wt.% SDS 0.12 wt.% SDS  
3 wt.% PI

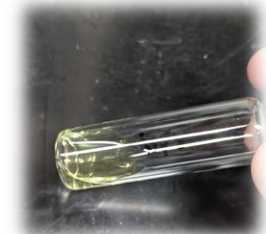


Foamed formulation

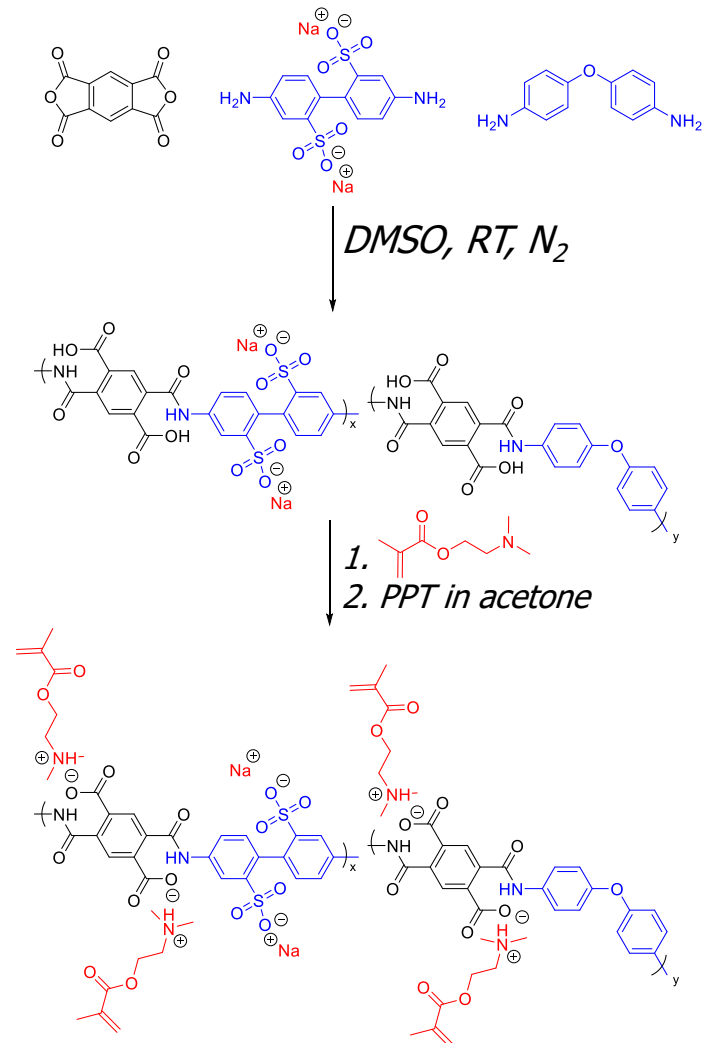
# Synthesis and neutralization of sulfonated polyamic acid (sPAA) with photolabile amine provides route to crosslinkable polymer surfactants

## Simplified synthetic route

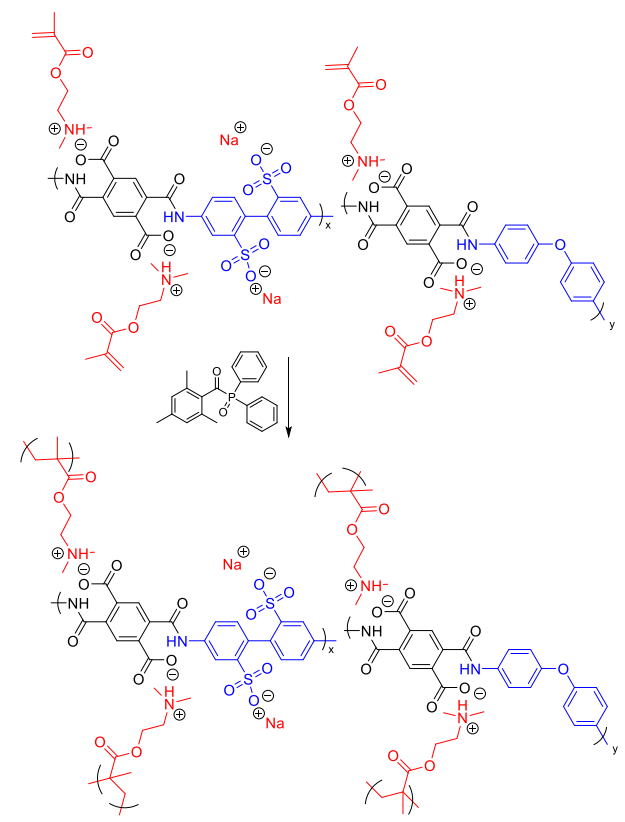
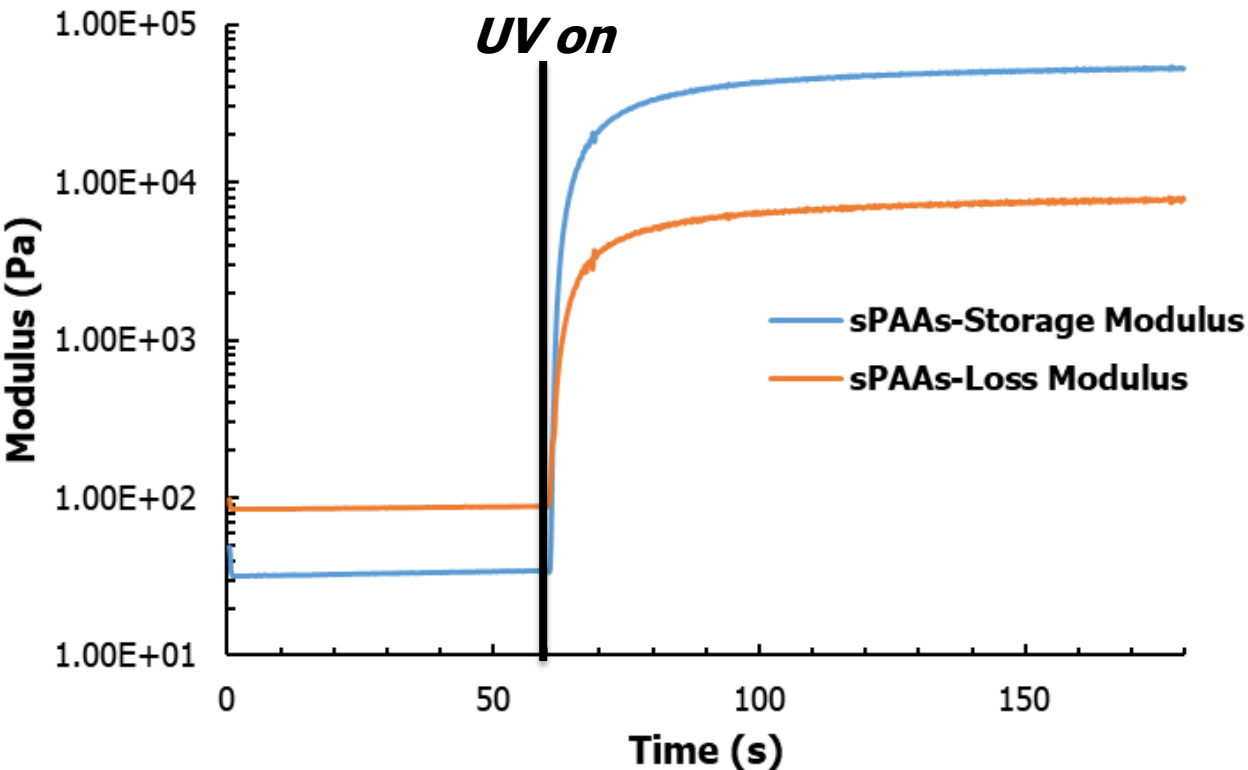
- Require diminished sulfonation for water dispersibility
- Neutralization of poly(amic acid) with various basic molecules allows for tuning of surfactant performance
- Inclusion of polymerizable unit may enable gel formation during flame suppression
- Exploring additional pathways based on backbone surfactant tethering



4 wt. % sPAAs in H<sub>2</sub>O

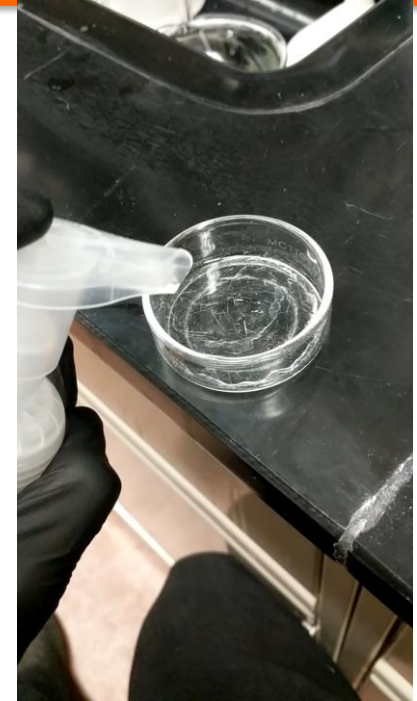
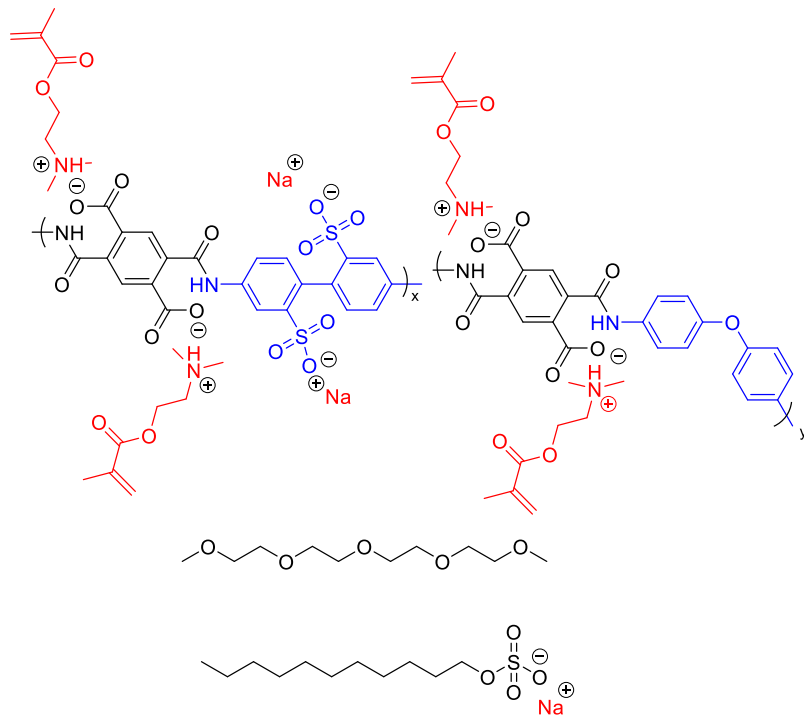


# High wt.% loading of sPAAs with photoinitiator permits photocrosslinking of fully aromatic polymer from water



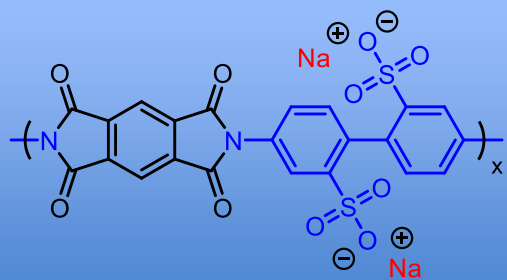
- 20 wt.% sPAAs in DI water
  - 2.5 wt.% TPO relative to sPAAs
- **1.3 s crossover time**

# Formulating sPAAs with alkyl surfactant, NaCl and glycolic ether enable production of stable foam

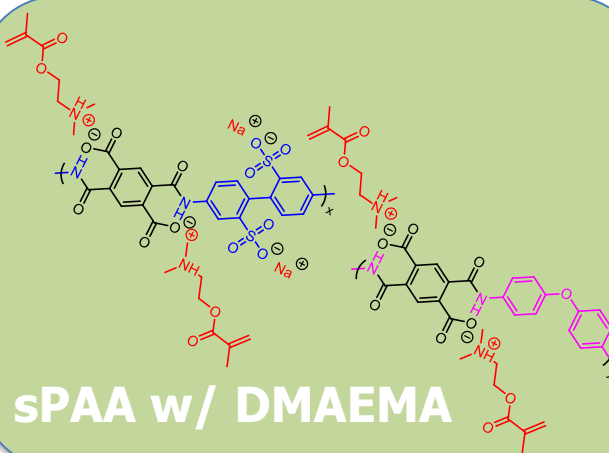


- Solution contains 4 wt.% sPAAs, 1 wt.% SDS, 1 wt.% NaCl and 1 wt.% tetraethylene glycol dimethyl ether in DI water
  - **Foam exhibited stability for > 30 min in petri dish**
- ✓ ER and DT reported are similar to Gen 1, if not marginally better

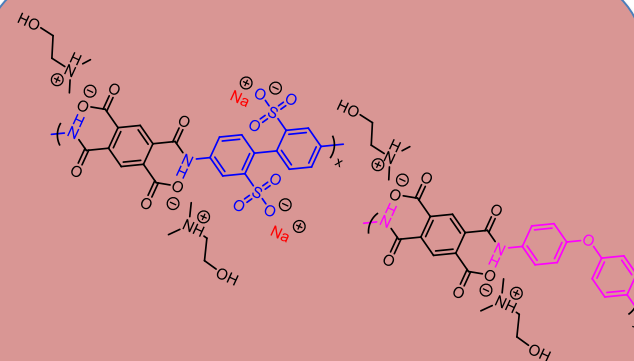
# Numerous polyimide/ poly(amic acid) “generations” attempt to combat liquid fuel fires



**sPI**



**sPAA w/ DMAEMA**



**sPAA w/ DMAE**

## Polymer Formulation

## Description

Generation 1

3 wt% sPI, 0.15 wt% SDS

Generation 1, revision 1

6 wt% sPI, 0.15 wt% SDS

Generation 2

3 wt% sPAAs w/ DMAEMA, 0.3 wt% SDS

Generation 3

3 wt% sPI, 0.15 wt% SDS, 0.3 wt% MTPP-Br,  
0.3 wt% NaCl

Generation 4

3 wt% sPAAs w/ DMAE, 0.15 wt% SDS

Generation 5

3 wt% sPAAs w/ DMAE, 0.15 wt% SDS, 1 wt%  
MTPP-Br

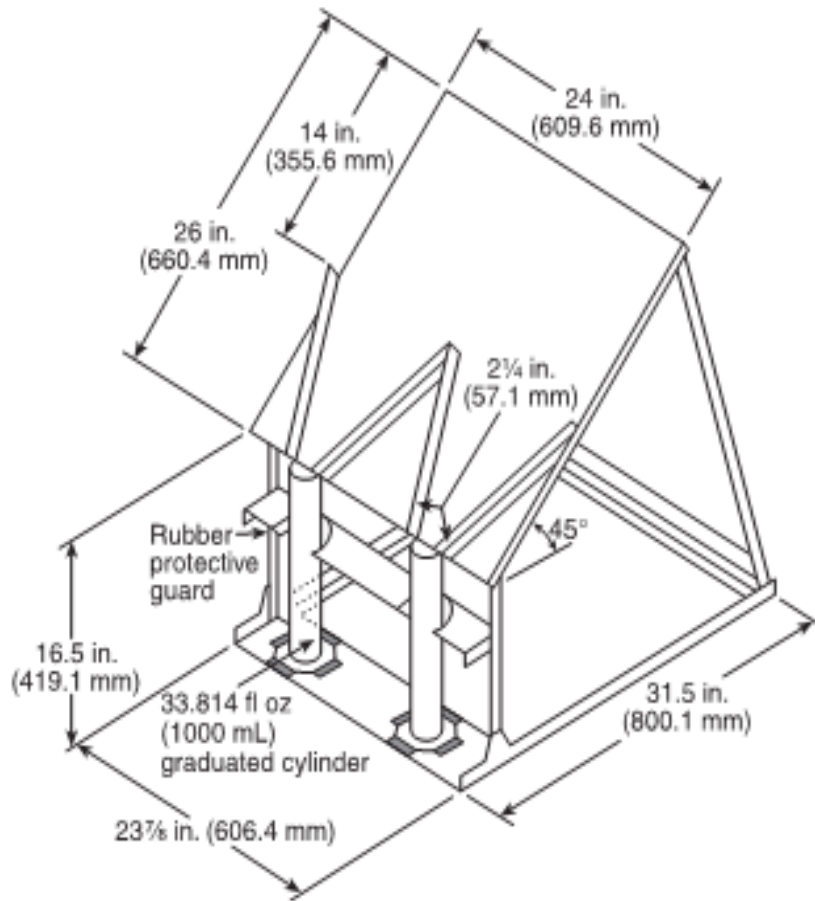
Generation 6

3 wt% 40:60 sPI (Gen1): sPAAs w/ DMAE  
(Gen4), 0.15wt% SDS

Generation 7

3wt% 50:50 sPAAS with DMAEMA (Gen2): sPAAs  
w/ DMAE (Gen4), 0.3 wt% SDS

# Measurement of foam expansion/ drainage conducted in accordance NFPA 412



NFPA 412- "Standard for Evaluating Aircraft Rescue and Fire-Fighting Foam Equipment"



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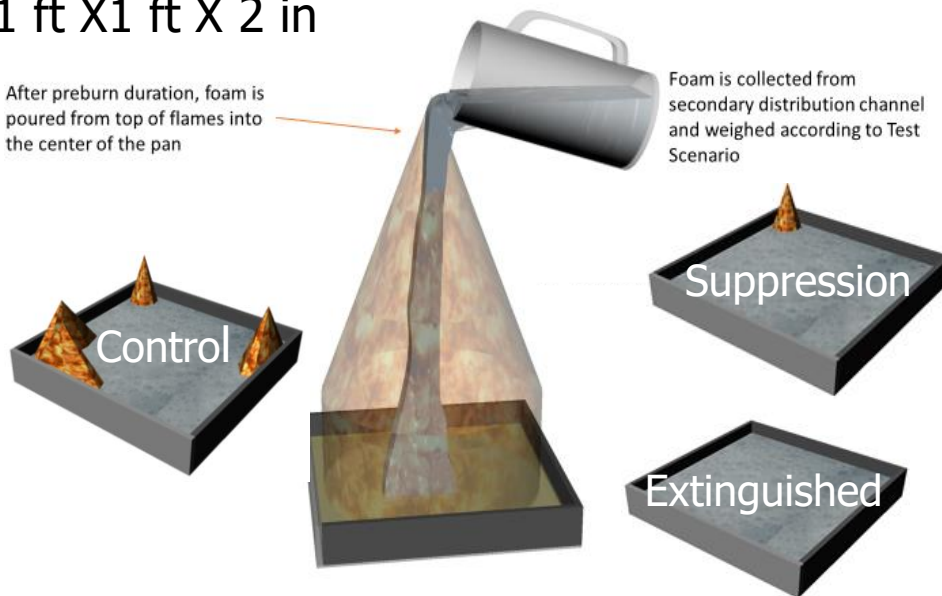
- **AFFFs are tested against a very strict US Military requirement- The "Mil Spec"- MIL-F-24385F**
  - Drainage Time- maximum 25% drainage in 2.5 min
  - Expansion Ratio- >5, foam volume 5x greater than liquid volume
  - Foam sprayed from the 2 GPM MilSpec nozzle at 4-6 ft
  - Weight of the cylinder measured to determine expansion ratio of the foam, quotient of the volume (mL) and the mass (g)

# Small scale testing at Jensen Hughs provides platform for foam screening

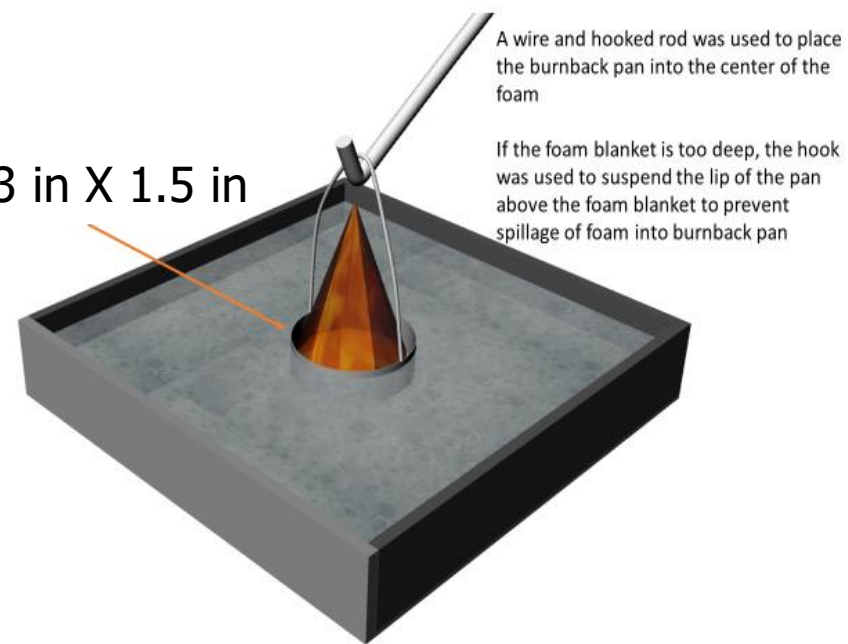
Test Class (Severity)	MIL-SPEC Pool Fire Test Basis	Pre-burn Time (s)	Foam Added for Ext. (g)	Foam Added After Ext. (g)	MIL-SPEC Test Basis
A (Least)	28 ft <sup>2</sup>	10	405	None	90 seconds of 2 GPM foam applied to 28 ft <sup>2</sup> pool fire

1 ft X 1 ft X 2 in

After preburn duration, foam is poured from top of flames into the center of the pan



3.3 in X 1.5 in



# Initial Foam Testing of Generation 1, meets MIL-SPEC ER/DT

## Foams tested using MIL-SPEC nozzle against MIL-F-24385F requirements<sup>2</sup>

- Max 25% drainage, 2.5 min
- Expansion ratio  $\geq 5$

### Average 25% Drainage

- $3.80 \pm 0.08$  min

### Average Expansion Ratio

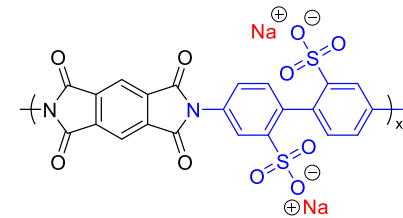
- $6.93 \pm 0.16$

### Burnback

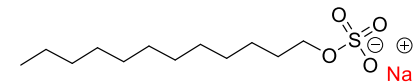
- Some suppression but low fluidity



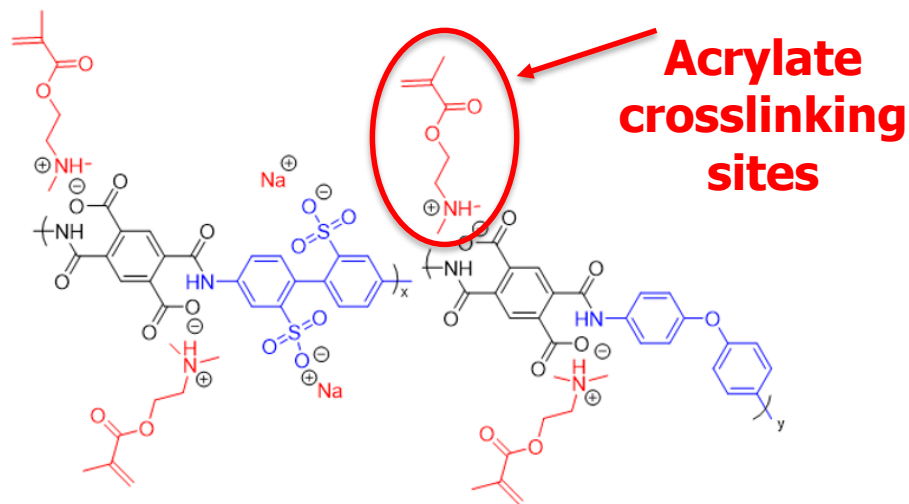
**3 wt.% PI**



**0.12 wt.% SDDS**



# Generation 2 foam crosslinks with heat, delaying ignition time and imparting fire control

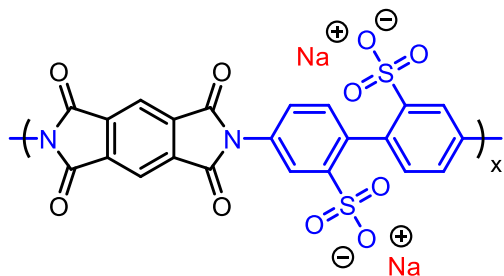


## Key Learnings of Gen 2 route:

- Simplified one-step synthetic strategy enables large scale
- **Cross-linking** of polymer exposed to higher radiant heating improves ignition resistance
  - Rapid control in fire test
- Only small flamlets exist on foam surface and edges after control
- Next Generations involve further modification of cationic site balance
  - Thermal stability
  - Gas phase interactions



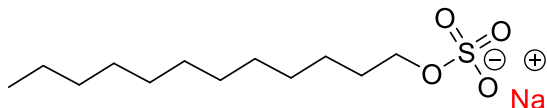
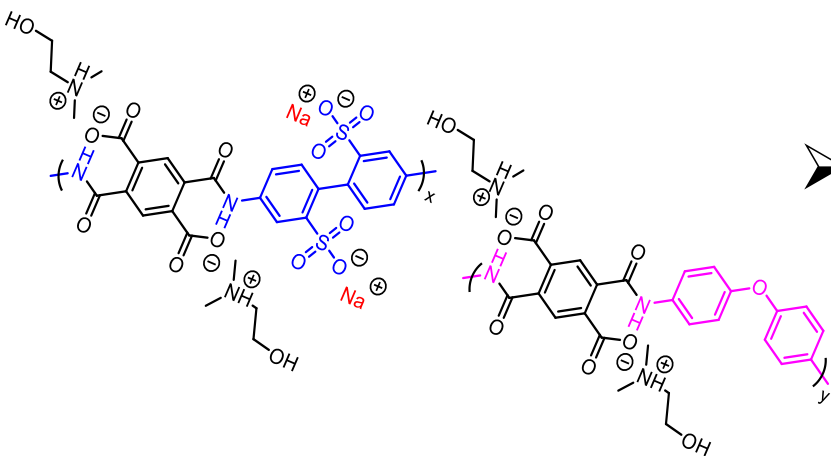
# Generations 6 and 7 are successful in extinguishing fire



## ➤ Generation 6

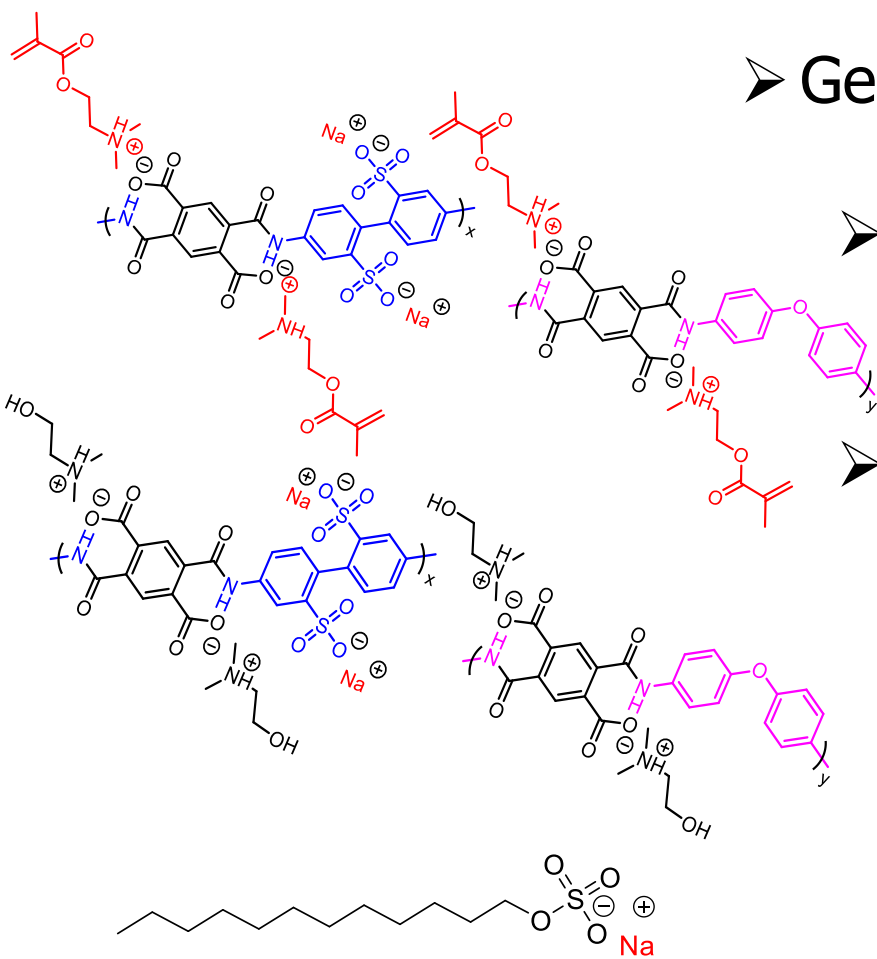
➤ Extinguishment:  
25 sec

➤ 25% Burnback:  
20 sec



40 sPI:60 sPAAs; 0.15 wt% SDS

# Generations 6 and 7 are successful in extinguishing fire (Cont.)



## ➤ Generation 7

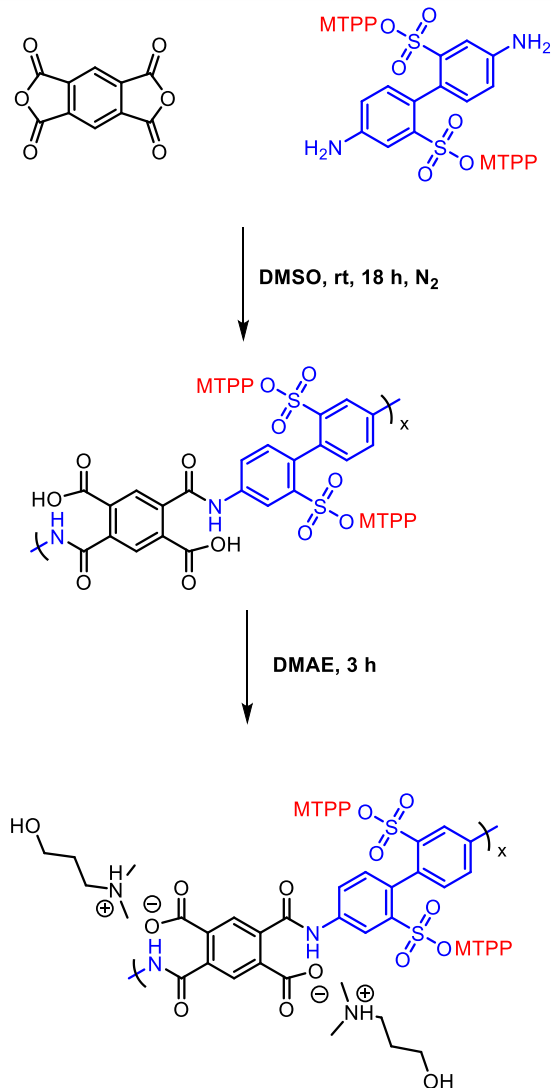
➤ Extinguishment:  
55 sec

➤ 25% Burnback:  
15 sec

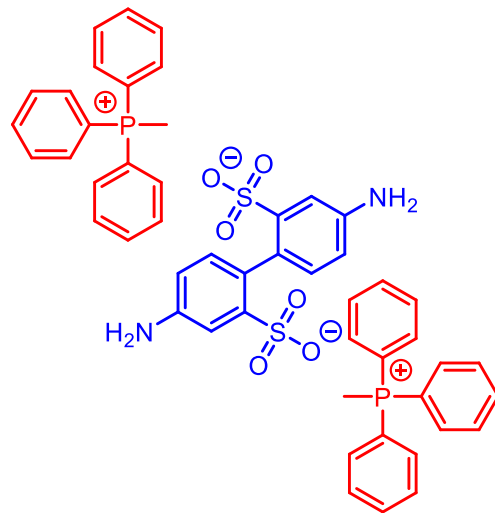


40 sPI:60 sPAAs; 0.15 wt% SDS

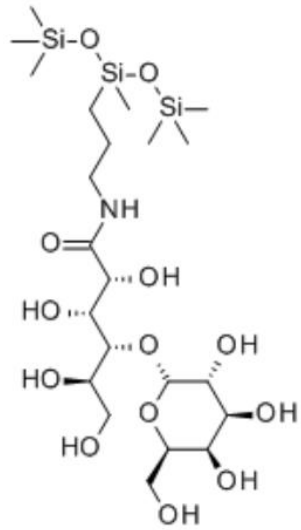
# Future Directions: Neutralization of sPAA with DMAE enables water solubility with phosphonium incorporation



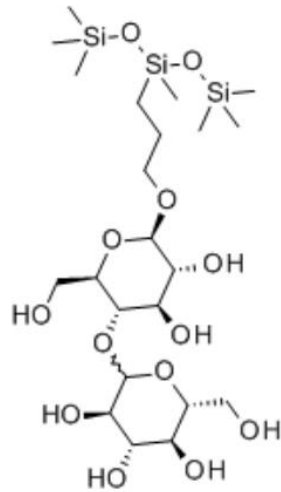
- Allows for simpler synthetic route with more control, modularity and potential added flame retardance with novel BDSA monomer
- Can vary mol% of phosphonium widely
  - Can combine with other types of monomers without hindering solubility
  - Aligns with SERDP trajectory



# Future Directions: Siloxane based foams to be another promising platform for fluorosurfactant replacement



Surfactant 1



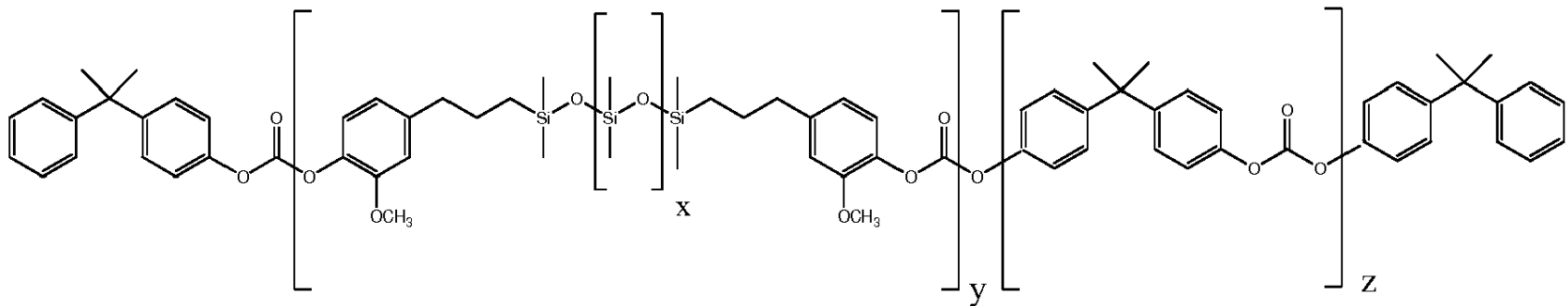
Surfactant 2

## Siloxanes and siloxane surfactants

- surface/ interfacial properties
- flame retardancy
- environmental friendliness

## Siloxane based foams **out-performed** other commercially available fluorine-free foams

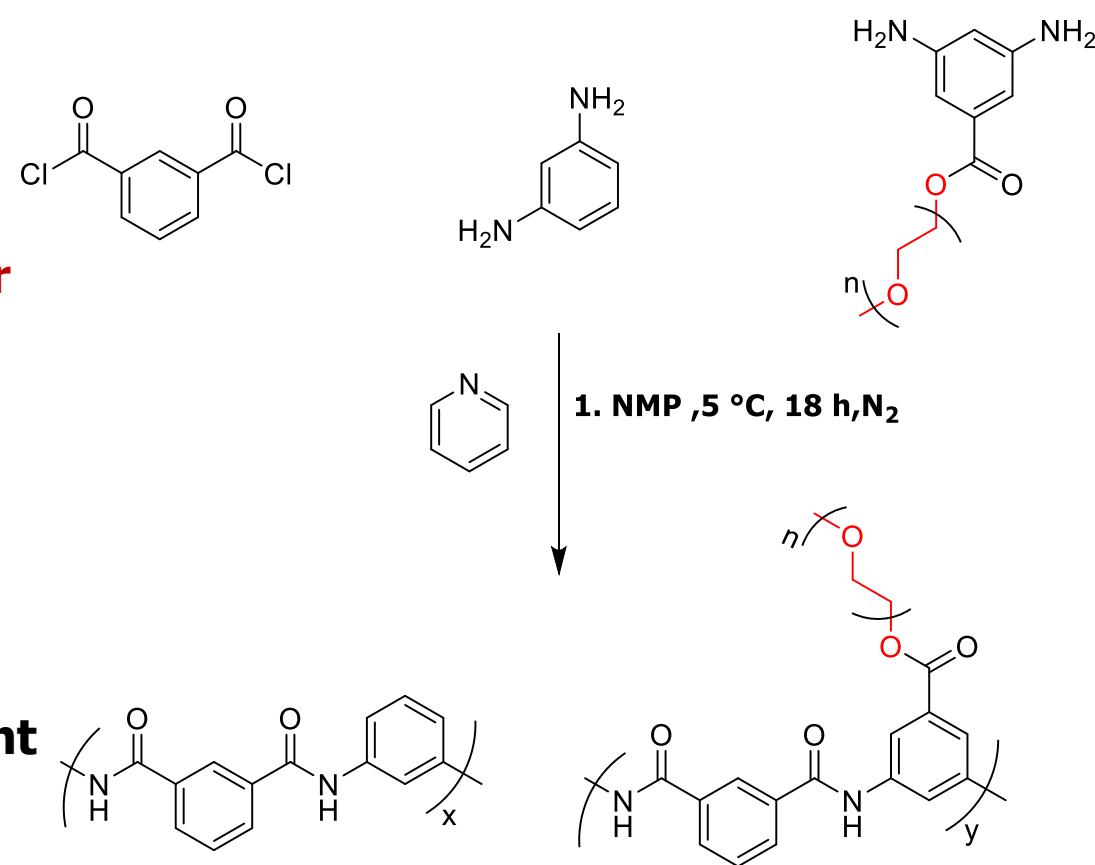
- Not as good as AFFF however



# Future Directions: Employment of grafted PIs as polymeric surfactants may improve flame suppression

## Nomex (*meta*-aramid) exhibits fantastic flame resistance<sup>1</sup>

- **Coupling with graft monomer may produce polymeric surfactant**
- Possible route to improved flame suppression
- **Tuning of graft density and composition dictate surfactant performance**
- Necessitates investigating toxicology of degradation products



1. Foo, C. C.; Chai, G. B.; Seah, L. K. *Compos. Struct.* **2007**, *80*(4), 588–594.

# Sulfonated polyimides and poly(amic acids) provide a promising platform for AFFF replacement

## ➤ Design of commercially viable synthesis

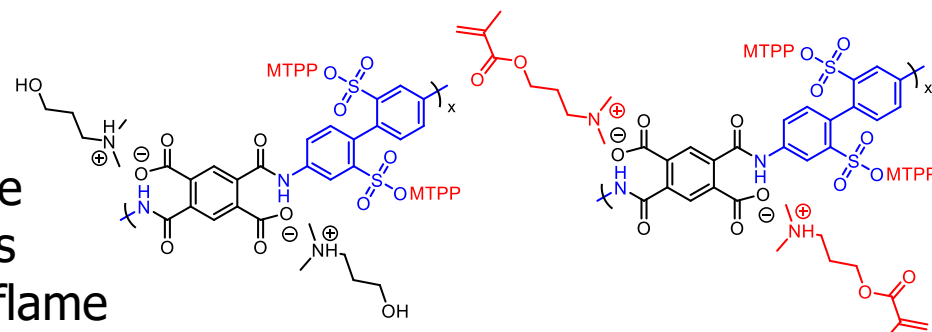
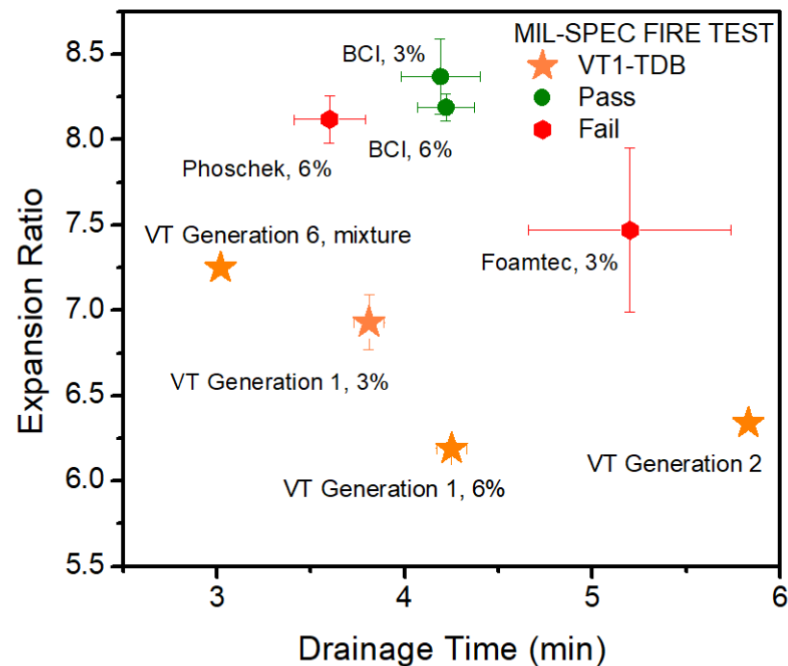
- Commercially Available Starting Materials
- Existing Reactor Technology
- Existing Industrial Partnerships in place
- Modular polymers → facile customization

## ➤ Establishment of foam evaluation protocol

- Expansion ration, drainage time, burnback, stability evaluated at JH
- Ecotoxicology evaluated at Army EDRC

## ➤ Future Directions include additional modification

- Varying crosslinker content
- Phosphonium cations for added flame resistance and gas phase interactions
- Siloxane segmented copolymers for flame resistance and interfacial activity



# Acknowledgements



MEETING DOD'S ENVIRONMENTAL CHALLENGES



Macromolecules  
Innovation Institute  
*At the intersection of science, engineering, and society*



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