Environmentally benign-phosphorous polymer(s) based fire suppression additives via an intumescence mechanism
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Naval Air Warfare Center Weapons Division (NAWCWD)

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14. ABSTRACT
The technical objectives of this project are listed below:
- The objective(s) of this one-year limited scope proposal (FY22/23):
  - Synthesize and characterize the flame suppression properties of phosphonate-based polymer(s) in a fluorine-free aqueous film forming foams (AFFF) formulation
  - Test the hypothesis that an “intumescence firesuppression mechanism” can be achieved
  - Meet the fire-extinguishing requirements found in performance specification fire-extinguishing agent, aqueous film forming foam liquid concentrate for fresh and seawater MIL-PRF-24385(SH) w/int. amendments

15. SUBJECT TERMS
AFFF, PFAS, toxicology, AFFF alternatives, PFAS-free firefighting formulations, developing new replacements

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Project Team

- PI: Peter Zarras (NAWCWD)

  Co-Performers:
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- Patrick Fedick, Elise Tseng (NAWCWD)
- Lawrence Baldwin (NAWCWD)
- Gregory S. Ostrom (NAWCWD)
- Eric Sievert (NAWCWD)
- Jason Lint (NAWCWD)
- Emily N. Reinke: US Army Public Health Center (APHC)

Background

- ✓ Year Project Initiated: FY2022
- ✓ Original Statement of Need: “Functional Additives and Foam Formation to Enhance PFAS-Free Fire Suppressants for Military Use”

Technical Objectives

The objective(s) of this one-year limited scope proposal (FY22/23):

- Synthesize and characterize the flame suppression properties of phosphonate-based polymer(s) in a fluorine-free aqueous film forming foams (AFFF) formulation
- Test the hypothesis that an "intumescence fire-suppression mechanism" can be achieved
- Meet the fire-extinguishing requirements found in performance specification fire-extinguishing agent, aqueous film forming foam liquid concentrate for fresh and seawater MIL-PRF-24385(SH) w/int. amendments

Technical Approach

Task 1:
Synthesis/Characterization of Monomers and Polymers

Task 2:
Toxicology Studies of Proposed Structures

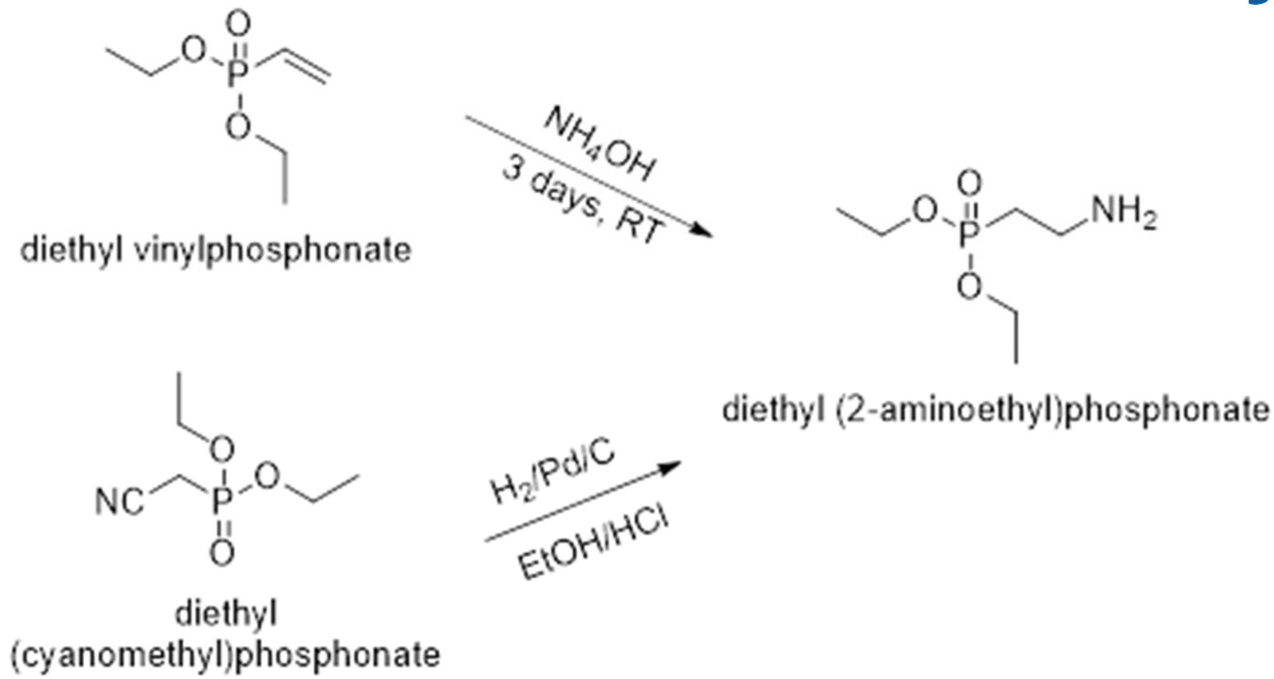
Task 2:
Completed by APHC

Task 3:
Formulations based on Poly(Phosphonate) Derivatives

Task 4:
Fire Performance Testing

Task 5
Transition to Full SERDP Program

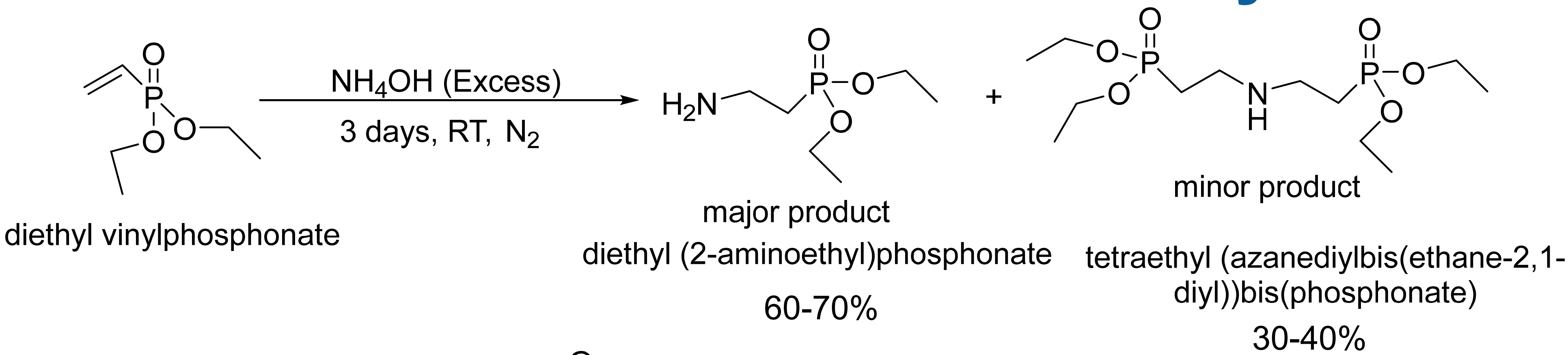
Task 1: Synthesis/Characterization of Intermediates/Monomers and Polymers

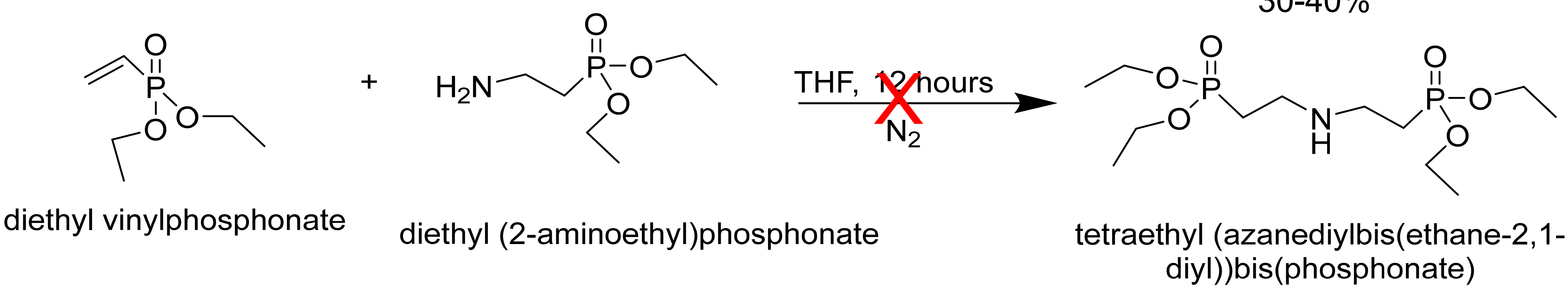


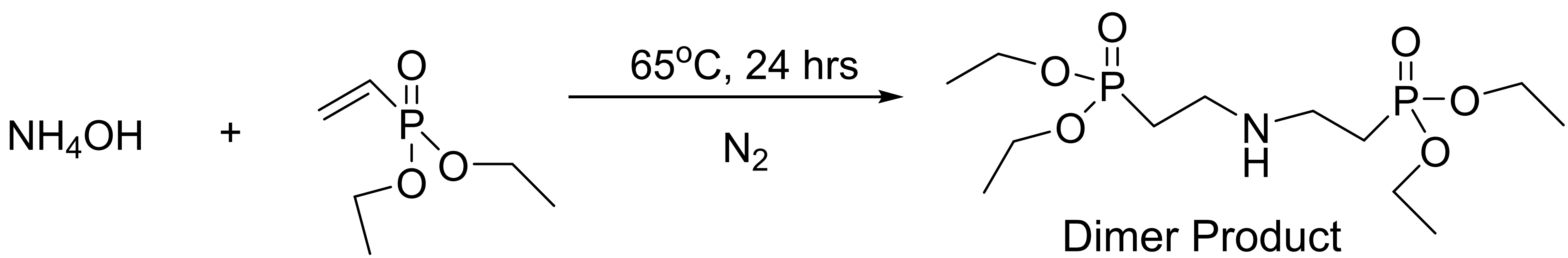
- Synthesis of the diethyl(2-aminoethyl)phosphonate via 3 day rx. successful
- Synthesis of the diethyl(2-aminoethyl)phosphonate via hydrogenation of the diethyl(cyanomethyl)phosphonate unsuccessful

D. M. Weekes, C. F. Ramogida, M. De g. Jaraquemada-Pelaez, B O. Patrick, C. Apte, T. I. Kostelnik, J. Cawthray, I. Murphy, C. Orvig, *Inorganic Chemistry*, **55(24)**, 12544-12558 (2016)
D. Marciani, B. Smolkin, H. Rotter, I. Columbus, S. Pittel, Y. Ophir, A. Pevzner, *Microporous and Mesoporous Materials*, **300**, 110-134 (2020)
M. Easson, B. Condon, M. Yoshioka-Traver, S. Childress, R. Slopek, J. Bland, T. M. Nguyen, S. E. Chang, and E. Graves, *AATCC Review*, **11(6)**, 60-66 (2011)
J. Ekke, U. Lehman, *Beilstein Journal of Organic Chemistry*, **5(72)** (2009)

Task 1: Synthesis/Characterization of Intermediates/Monomers and Polymers



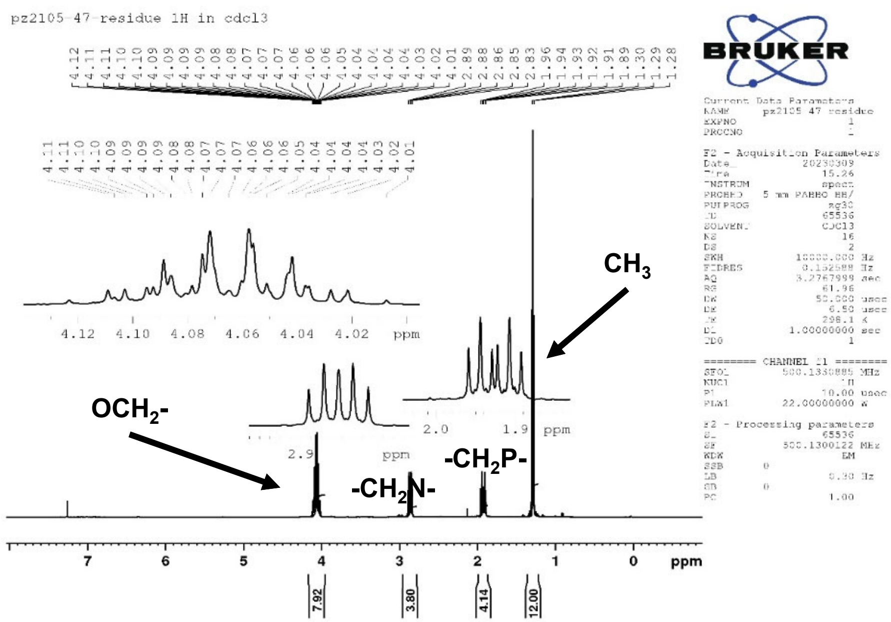


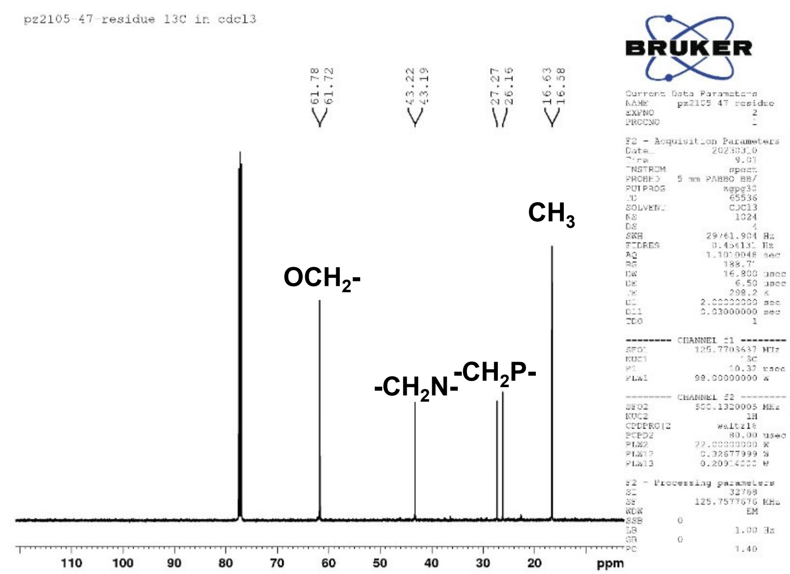


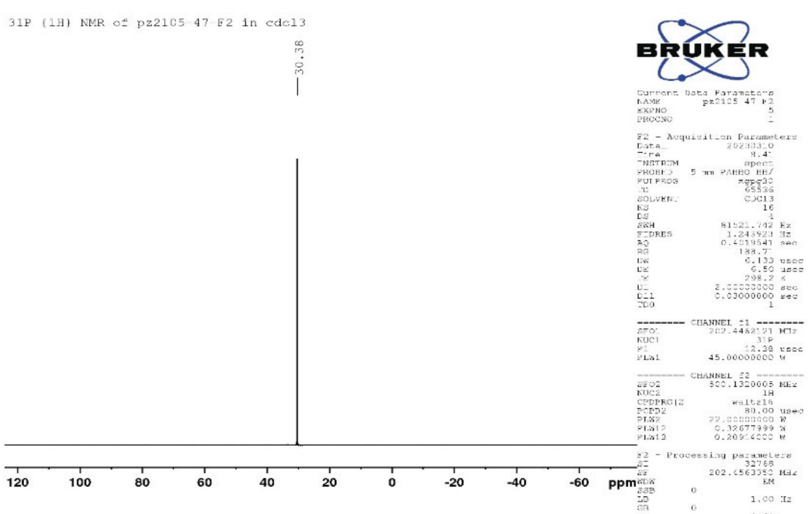
Chemical Formula: $C_{12}H_{29}NO_6P_2$

Elemental Analysis: C, 41.74; H, 8.47; N, 4.06; O, 27.80; P, 17.94

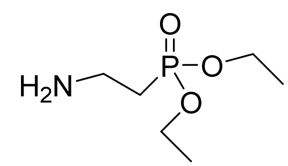
Task 1: Synthesis/Characterization of Intermediates/Monomers and Polymers



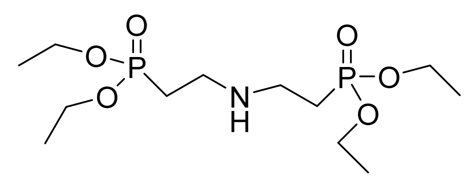




GC/MS for mono-substituted product = 181



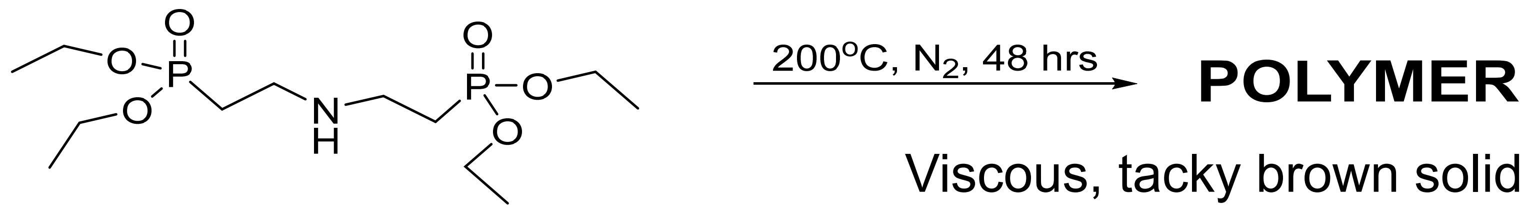
GC/MS for dimer = 345



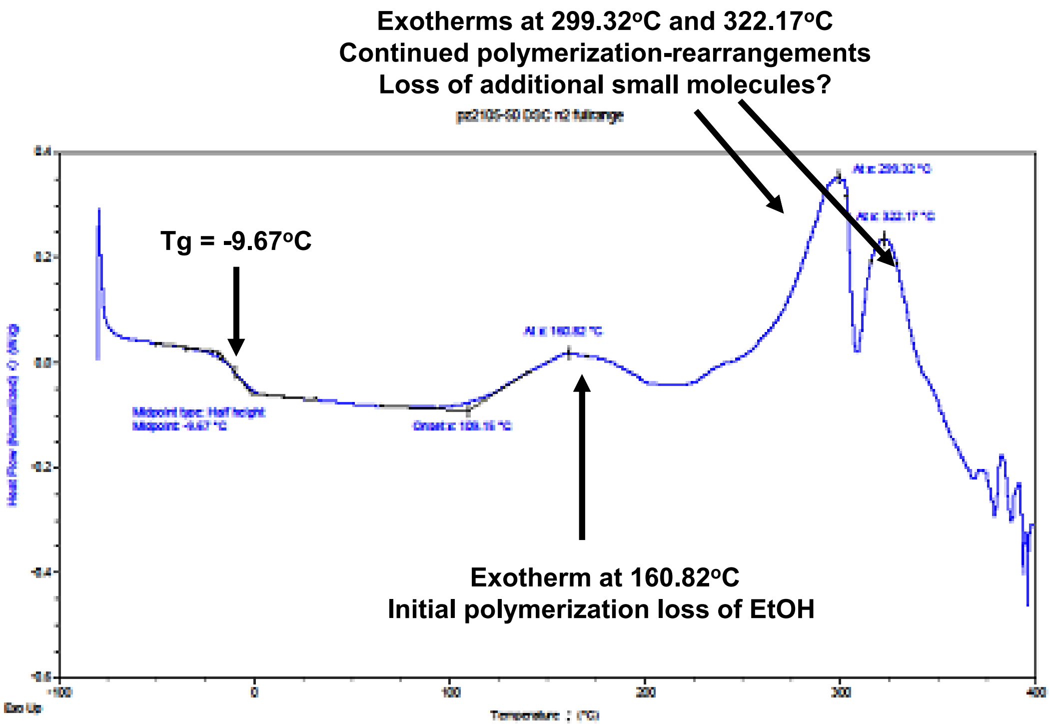
Task 1:
Synthesis of the Tetraethyl(azanediylbis (ethane-2,1-diyl)bis(phosphonate) (Dimer product)

Ammonium Hydroxide 28-30 wt.%	Diethylvinyl phosphonate	Conditions	Recovered	Appearance
1 equivalents	2 equivalents	65^{o}C 24 hours	Dimer + trimer (M=508)	Light yellow oil
1.65 equivalents	2 equivalents	65^{o}C 24 hours	Dimer + Mono-substituted product	Light yellow oil
Scale-up of rx.	Scale-up of rx.	65^{o}C 24 hours	Dimer obtained exclusively via removal of Mono-substituted product via vacuum/heating Y=75-85%	Clear oil [Upon standing solid crystals form]

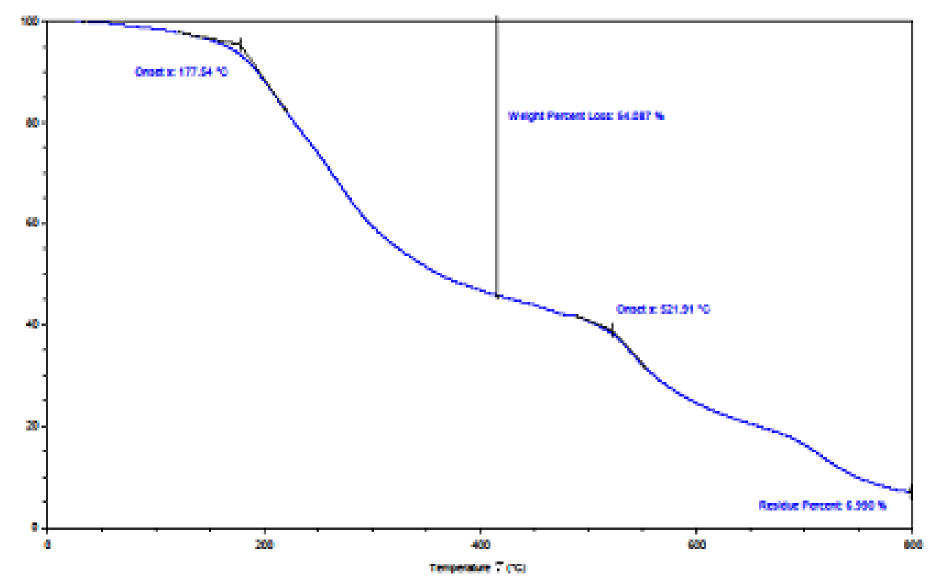
Task 1: Homopolymerization of Tetraethyl(azanediylbis-(ethane-2,1-diyl)bis(phosphonate) (Dimer product)



Viscous, tacky brown solid, Y= 90%

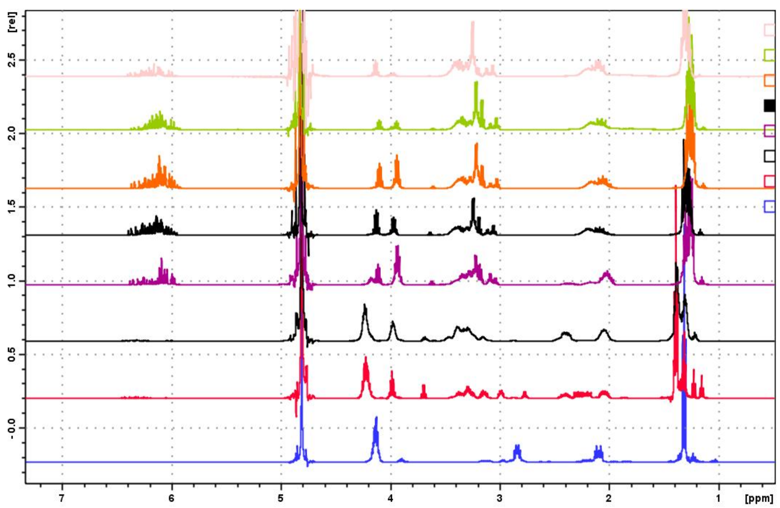


DSC Figure of Homopolymer

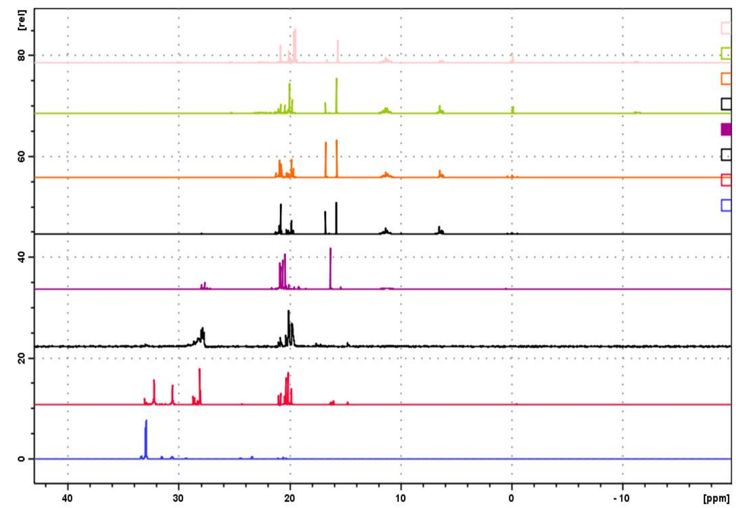


TGA Figure of Homopolymer

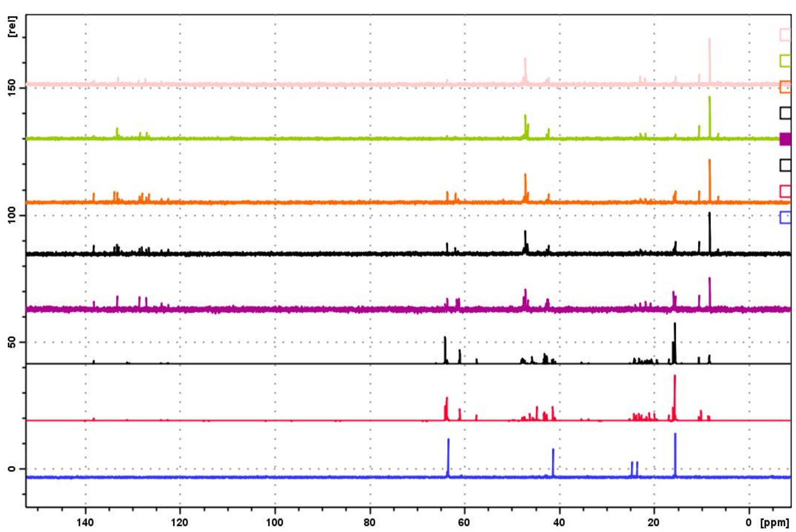
Task 1: NMR Characterization of Homopolymer



1H NMR Stack plot



31P NMR Stack Plot



13C NMR Stack plot

Stackplots are (going from bottom to top)

T= 0 minutes (start)

T=200^{o}C, N_2 blanket/Neat Polymerization

5 minutes

10 minutes

1 hr

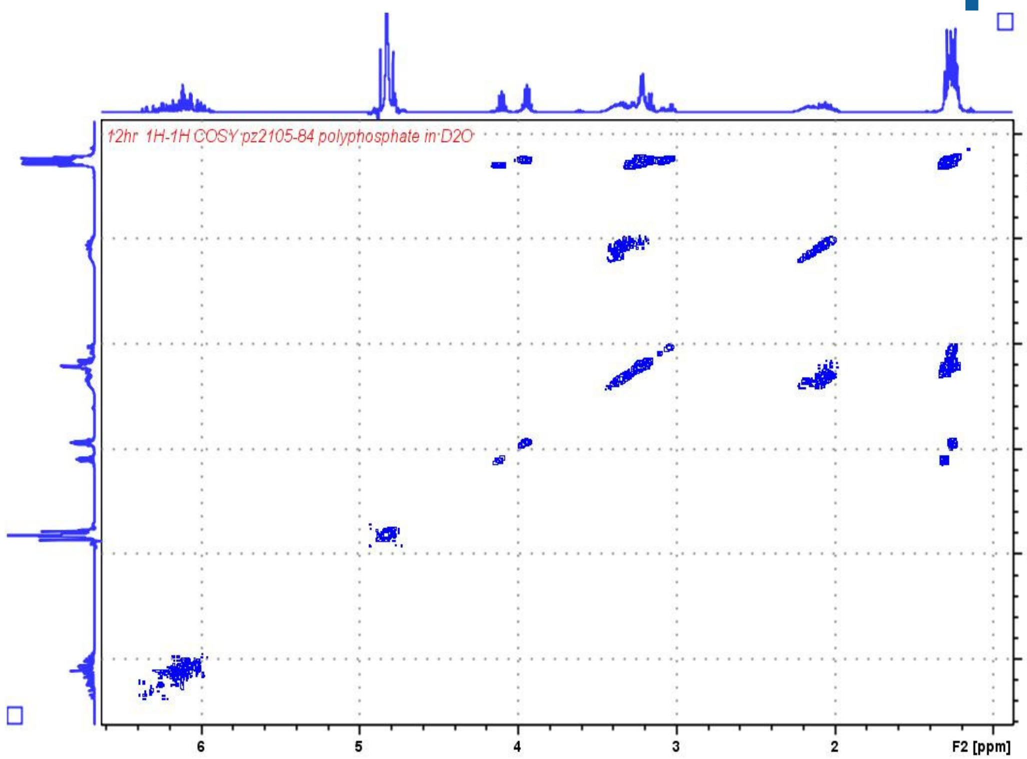
6 hr

12 hr

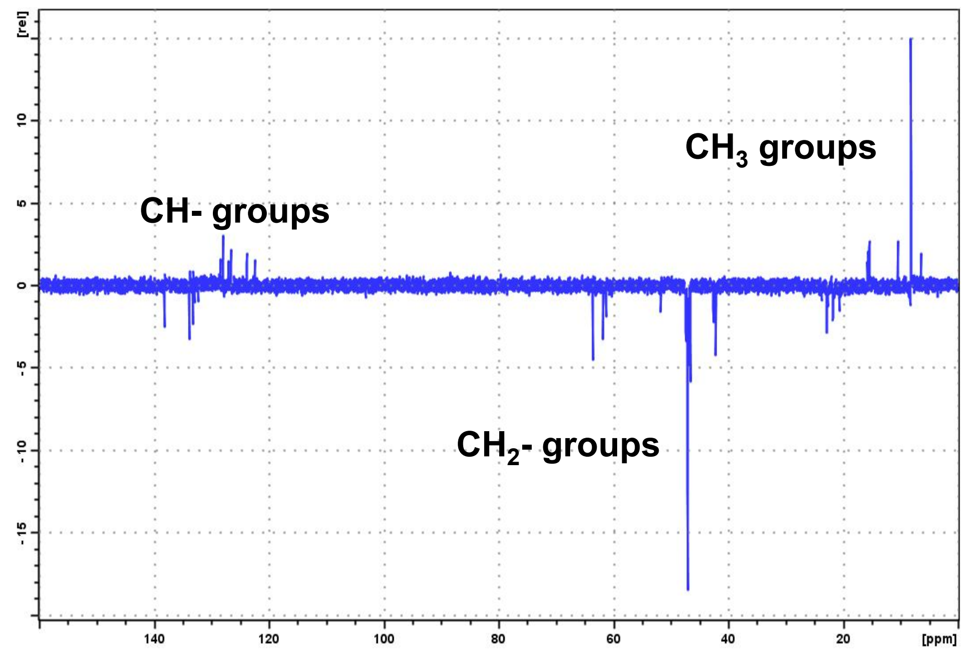
24 hr

36 hr

Task 1: NMR Characterization of Homopolymer



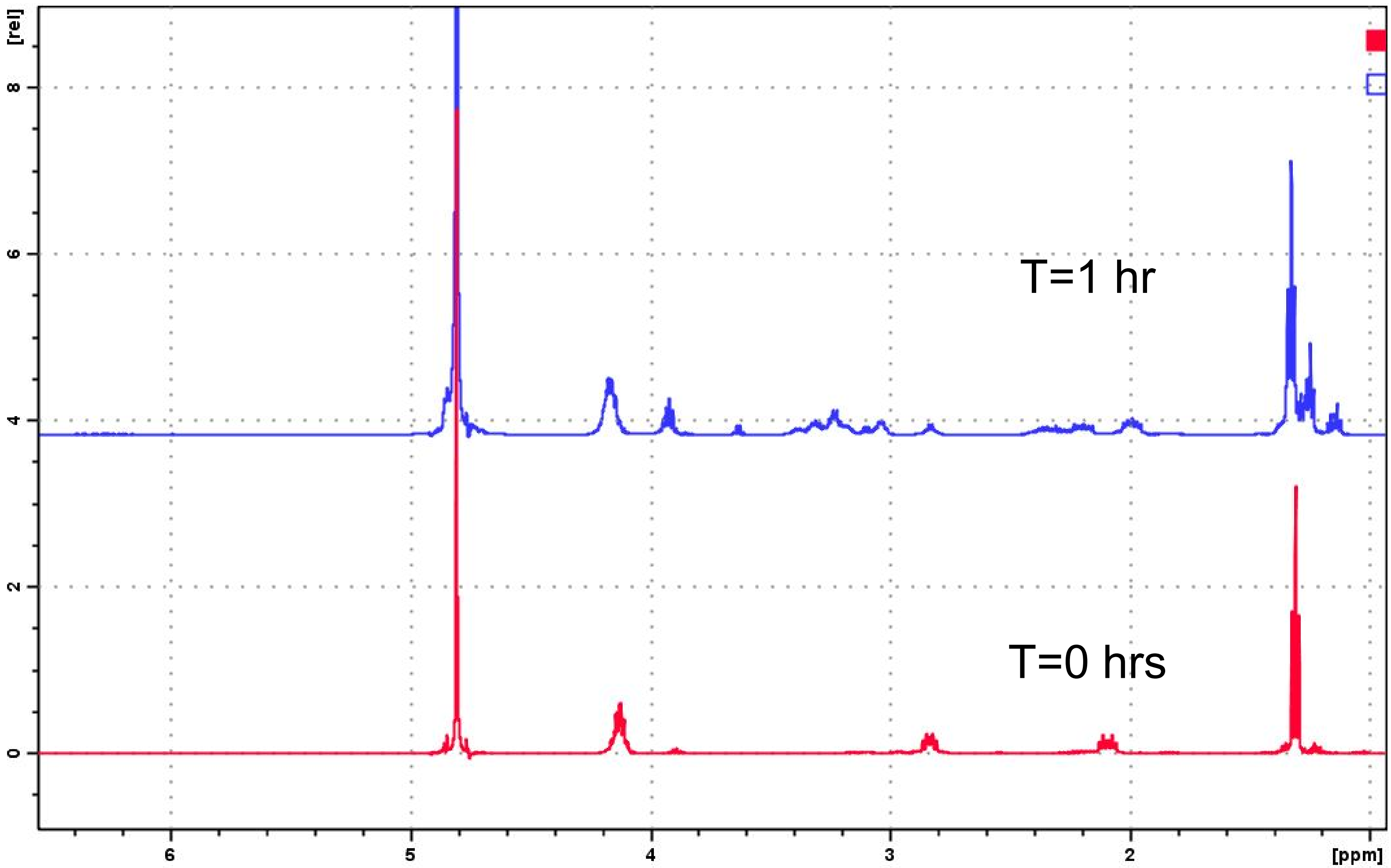
12 hr - 1H-1H COSY NMR Spectrum



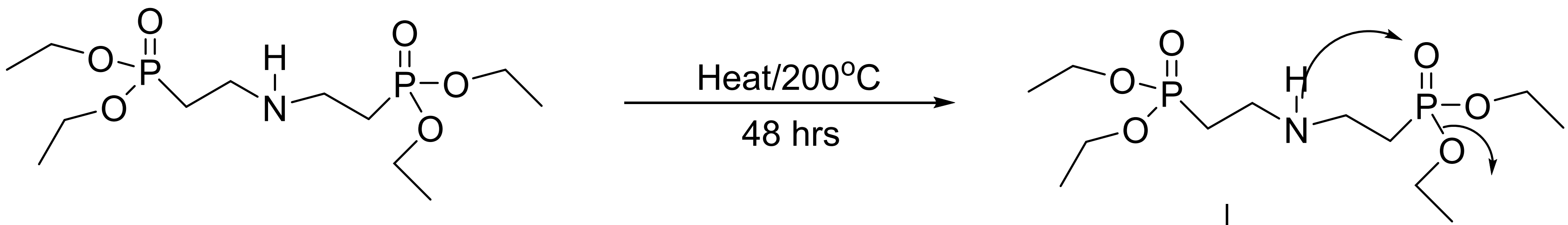
12 hr-13C DEPT NMR Spectrum

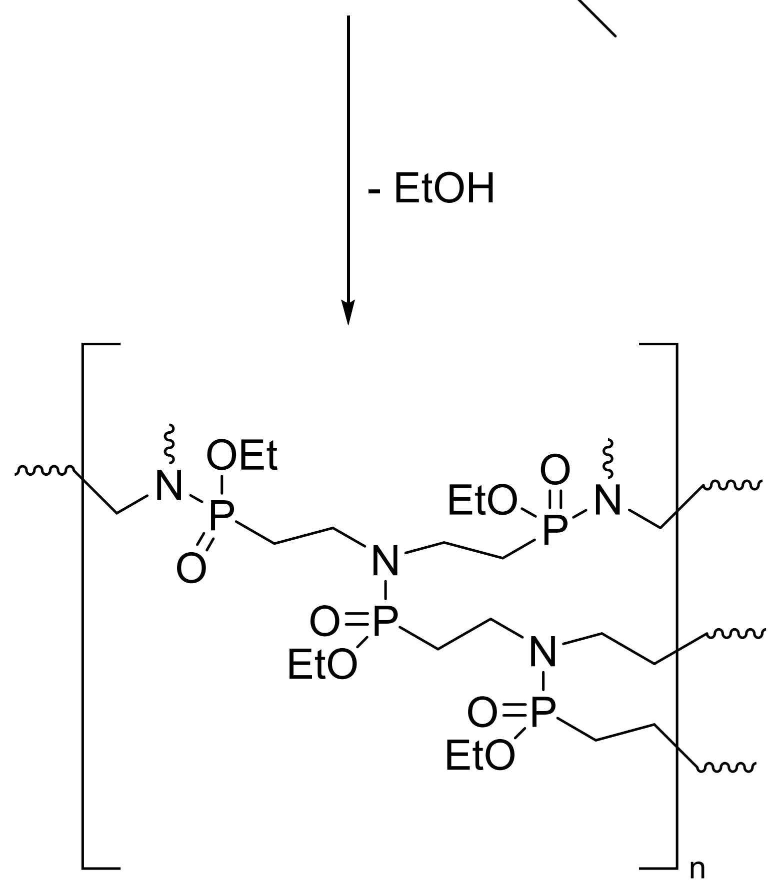
After an hour, alkene peaks are quite noticeable with their max signal being at 12 hours elapsed
These alkene peak intensities lower with continued heating. In general there are many compounds that lead to the final polymer
None have been identified
There appear to be phosphorus-alkene bonds and some ethoxy and N-alkyl groups are present as well

1H NMR Studies of Homopolymerization at 160°C for 1Hour



Task 1: Proposed Structure/Mechanism for Homopolymer





- ✓ Highly branched polymer structure?
- ✓ Very Soluble in DI water
- ✓ No solubility in common organic solvents

Task 3: Formulation Studies of Homopolymer

Formulation Based on Concentration (150 mL) Lasagna Pan
(12” x 9” steel baking pan) Fire Testing

Sample ID	DI Water (grams)	Glucopon 225 DK (BASF Product - APG Foamer) (Grams)	Homopolymer
Control Water	150	X	X
Glucopon 225DK control	143.5	5.0	X
Formulation #1	143.5	5.0	1.5
Formulation #2	143.5	5.0	1.5

- ✓ All reagents went into DI water <5 minutes
- ✓ 5 wt.% Alkylpolyglycosides (APG) used for initial fire suppression studies

Task 4: Fire Performance Testing Studies

Lasagna Pan Fire Testing

Test Setup

Water Control F-24 Fuel

Glucopon 225DK F-24 Fuel

Formulation #1 F-24 Fuel

Task 4: Fire Performance Testing Studies

Formulation #1 F-24 Fuel

Formulation #2 Gasoline (Ethanol-free) Fuel

Formulation #2 Gasoline (Ethanol-free) Fuel

Task 4: Fire Performance Testing Assessment

✓ **Test 1 (F-24 vs. Water)**

- There was no positive effect on fuel extinguishment and the fuel was snuffed out early by the test team to ensure the steel pan did not warp from the heat
- The fire was extinguished by the test team at 36 seconds

✓ **Test 2 (F-24 vs. Pz2105-71 Control Glu 225 DK)**

- Most of the agent was dumped onto the ramp within 6 seconds
- Small amounts of high expanded foam was sticking to the inside of the blender and was unable to be used
- The foam had some positive effects on the fire in the center of the fuel but did not extinguish the F-24 within the required 60 second requirement listed in the SERDP challenge
- This fire was snuffed out after 1 minute by placing a metal plate over the pan

✓ **Test 3 (F-24 vs. PZ2105-71 Formulation 1)**

- Most of the agent was dumped onto the ramp within 6 seconds
- Like observed in test 2, the foam ratio looked to be very high, resulting in small amounts of high expanded foam sticking to the inside of the blender
- The foam had more positive effects on the fire as compared to test 2 where there was more extinguishment in the center of the fuel and along some of the edges. Unfortunately, formulation one did not extinguish the F-24 within the required 60 seconds listed in the SERDP challenge
- This fire was snuffed out after 1 minute by placing a metal plate over the pan

✓ **Test 4 (Ethanol-Free Fuel vs. PZ2105-71 Formulation 2)**

- Most of the agent was dumped onto the ramp within 6 seconds. Like observed in test 2 and 3, the foam ratio looked to be very high, resulting in small amounts of high expanded foam sticking to the inside of the blender.
- The test team notices through the flames that there was a thick blanket of foam that extended the entirety of the fuels surface, but this foam did not suppress and lock in the fuel vapors allowing the fuel vapors to burn undeterred through the bubbles
- Formulation 2 did not extinguish the ethanol free fuel within the required 60 seconds listed in the SERDP challenge
- This fire was snuffed out after 1 minute by placing a metal plate over the pan

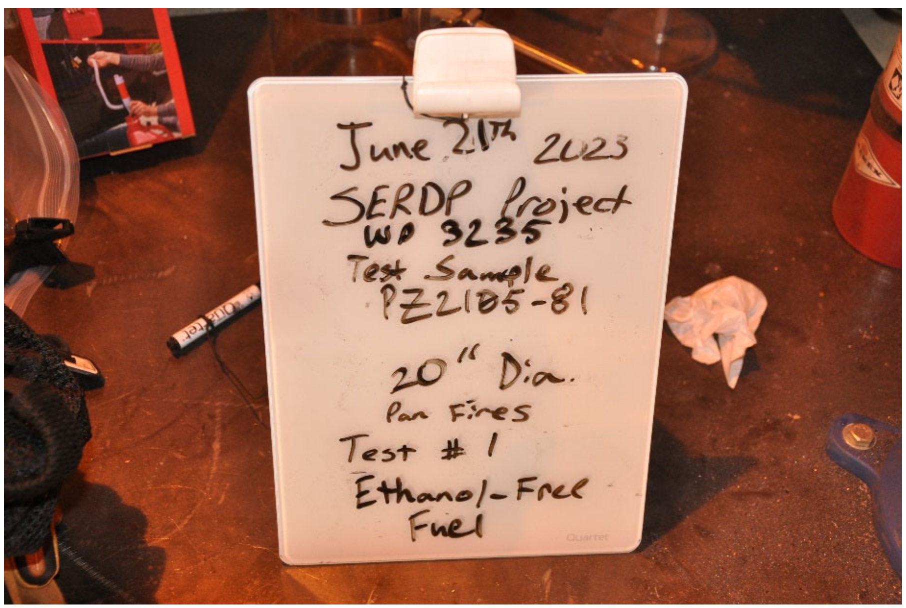
*** AFFF extinguishes this size fire in 10 seconds–performance standard**

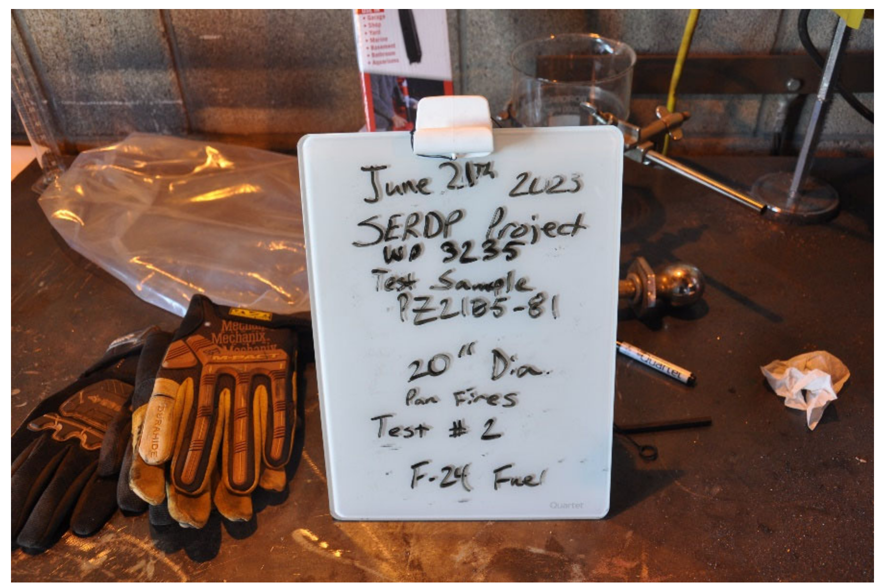
Task 3: Formulation Studies
5 gallon fluorine-free AFFF formulation

Concentrate Formulation (T= 100 mL)

Sample ID	DI Water (grams)	Glucopon 225 DK (grams)	Homopolymer (grams)
Formulation #1	30.8	36.0	33.2

The concentrate was diluted to 5 gallons using 18.8L DI Water
Fire testing was performed using a 20" diameter Pan Fire





Task 4: Fire Performance Testing Studies

Fire testing was performed using a 20” diameter Pan Fire

Formulation #1: Gasoline (ethanol-free) fuel

Formulation #1: F-24 fuel

Task 4: Fire Performance Testing Assessment

✓ **Test #1 Gasoline Ethanol-Free Fuel**

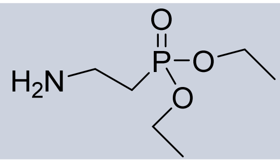
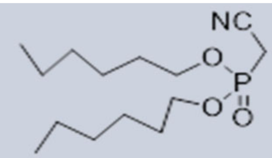
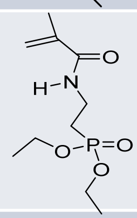
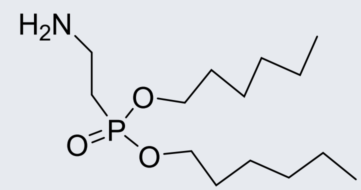
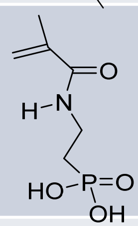
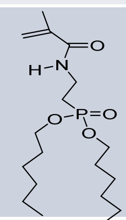
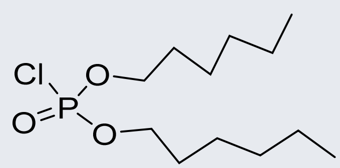
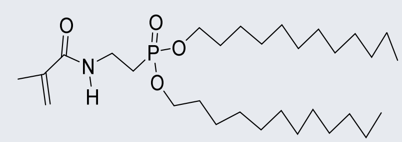
- As per the current fresh water MilSpec, testing with ethanol free fuel, the agent was allowed to flow onto the fuel and attack the fire for at least 60 seconds
- For this test, the test team allowed the agent to flow for an additional 30 seconds to see if the additional time would have made a difference
- This agent against the ethanol free liquid fuel had no effect on the fire and did not show signs of a reduced burn rate
- This test fire was snuffed out by the test team at the 90 second mark with the use of a steel cover to reduce the amount of oxygen to the fuel/fire

✓ **Test #2 F24 Fuel (JP8 without the corrosion inhibitors additives)**

- As per the current fresh water MilSpec, testing with JP8, the agent was allowed to flow onto the fuel and attack the fire for at least 30 seconds
- For this test, the test team allowed the agent to flow for an additional 30 seconds to see if the additional time would have made a difference
- This agent against the F24 fuel had no effect on the fire and did not show signs of a reduced burn rate
- This test fire was snuffed out by the test team at the 60 second mark with the use of a steel cover to reduce the amount of oxygen to the fuel/fire

*** AFFF extinguishes this size fire in ≤ 30 seconds–performance standard**

Structures Modeled for Toxicity Studies

Compound	Chemical Structure	Compound	Chemical Structure
Diethyl (2-aminoethyl)phosphonate [DEAP]		**Dihexyl (cyanomethyl) Phosphonate [DHCMP]**	
Diethyl (2-methacrylamidoethyl)phosphonate [DEMAP]		**Dihexyl (2-aminoethyl)phosphonate [DHAEP]**	
(2-methacrylamidoethyl)phosphonic acid [MAPA]		**Dihexyl (2-methacrylamidoethyl) phosphonate [DHMAEP]**	
Dihexyl phosphorochloridate [DEPC]		**Didodecyl (2-methacrylamidoethyl) phosphonate [DDMAEP]**	

Task 2: Toxicology/Modeling Studies of Proposed Structures

Chemical Substance	CAS RN
Diethyl (2-aminoethyl)phosphonate [DEAP]	41468-36-4
Diethyl (2-methacrylamidoethyl)phosphonate [DEMAP]	Not registered
(2-methacrylamidoethyl)phosphonic acid [MAPA]	45028-94-2
Dihexyl phosphorochloridate [DEPC]	Not registered
Dihexyl (cyanomethyl)phosphonate [DHCMP]	Not registered
Dihexyl (2-aminoethyl)phosphonate [DHAEP]	Not registered
Dihexyl (2-methacrylamidoethyl)phosphonate [DHMAEP]	Not registered
Didodecyl (2- methacrylamidoethyl)phosphonate [DDMAEP]	Not registered

Toxicity Data APHC

Compound	Acute Oral LD_{50} (mg/kg)	Chronic Oral LOAEL (mg/kg-d)	Inhalation LC_{50} (g/m3-h)	Dermal	Ocular	Development/ Reproduction	Genotoxicity	Carcinogenicity
DEAP	75.8	24.1	1.279	Mild irritant, negative sensitization	Severe irritant	Positive	Negative	Negative
DEMAP	340.5	20.5	2.5	Negative	Moderate	Negative	Negative	Negative
MAPA	6788.9	24.85	1.915	Negative	Moderate Irritant	Negative	Negative	Negative
DEPC	2744	172.98	4.065	Mild irritant	Negative	Negative	Negative	Negative
DHCMP	749.8	154.3	2.1	Mild irritant	Negative	Negative	Negative	Negative
DHAEP	1060.5	72.8	1.5	Mild irritant	Negative	Negative	Negative	Negative
DHMAEP	3294	44.6	2.66	Mild irritant	Negative	Negative	Negative	Negative
DDMAEP	9735	34.5	0.470	Mild irritant	None	Negative	Negative	Negative

Task 2: Toxicology Studies of Proposed Structures

Toxicity Assessment

Compound	Oral	Inhalation	Dermal	Ocular	Carcinogenicity
DEAP	Moderate	Moderate	Moderate	High	Low
DEMAP	Moderate	Low	Low	Moderate	Low
MAPA	Moderate	Low	Low	Moderate	Low
DEPC	Low	Low	Moderate	Low	Low
DHCMP	Moderate	Moderate	Moderate	Low	Low
DHAEP	Moderate	Low	Low	Low	Low
DHMAEP	Moderate	Moderate	Moderate	Low	Low
DDMAEP	Moderate	High	Moderate	Low	Low

Ecotoxicity Assessment

Compound	Aquatic	Terrestrial Invertebrates	Terrestrial Plants	Mammals	Birds
DEAP	Low	Unk	Unk	Moderate	Unk
DEMAP	Moderate	Unk	Unk	Moderate	Unk
MAPA	Moderate	Unk	Unk	Moderate	Unk
DEPC	High	Unk	Unk	Low	Unk
DHCMP	High	Unk	Unk	Moderate	Unk
DHAEP	Moderate	Unk	Unk	Moderate	Unk
DHMAEP	High	Unk	Unk	Moderate	Unk
DDMAEP	High	Unk	Unk	Moderate	Unk

Task 2: Conclusion of Toxicology Studies of Proposed Structures (APHC Assessment)

- ✓ The proposed chemicals for use in PFAS-free AFFF formulations generally have lower predicted toxicity compared to perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), two legacy PFAS compounds found at high levels at sites where AFFFs are frequently utilized

- ✓ A full comparison between the proposed polyphosphonate additives and all utilized PFAS in existing AFFF formulations is not feasible due to the large number of potential comparators

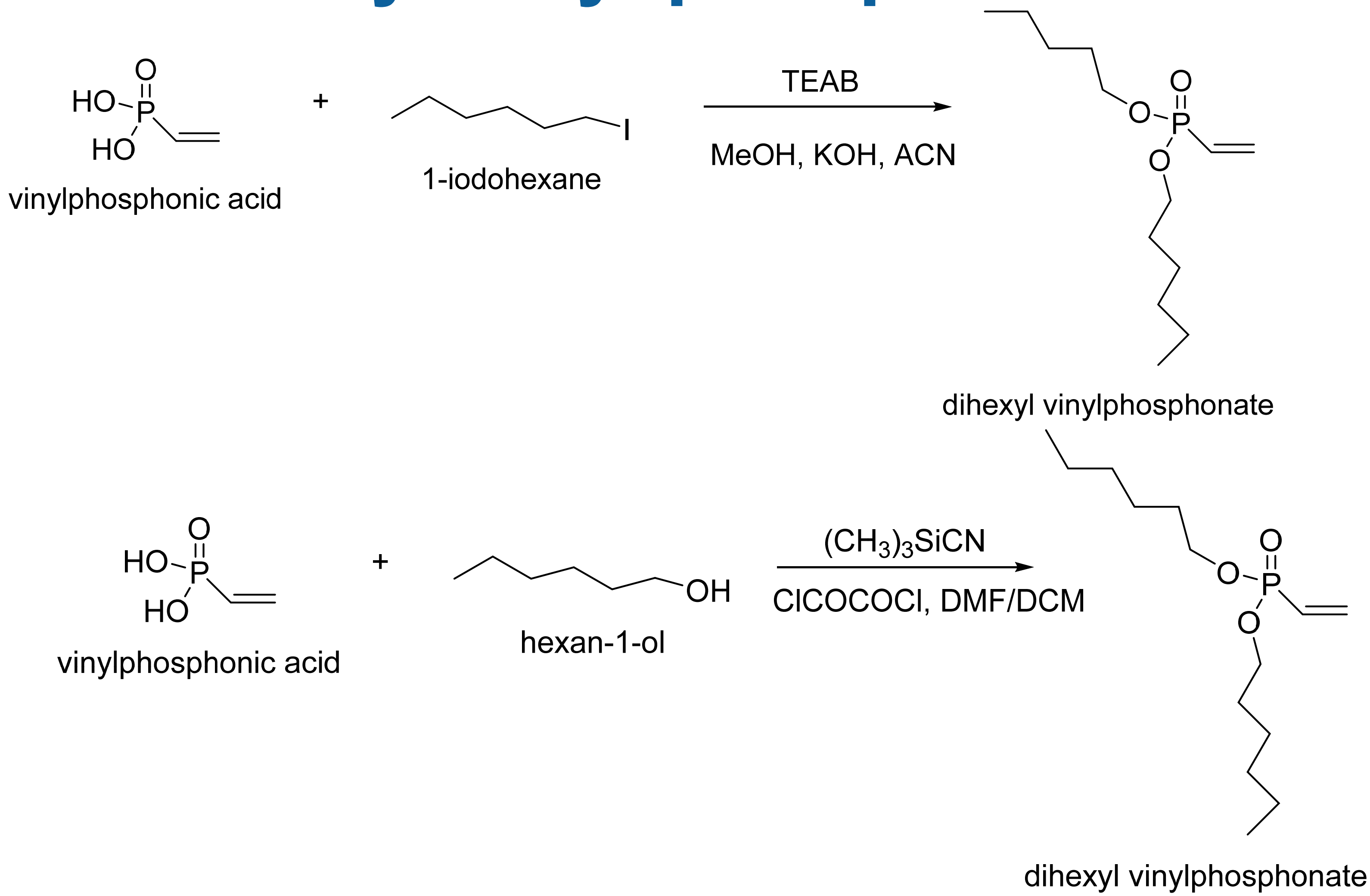
- ✓ PFOA and PFOS were selected due to the amount of data available on their toxicity

- ✓ In order to have a better understanding of the potential toxic effects of these additives, *in vitro* testing is highly recommended for any candidate that is proposed for additional performance assessment by the PI of this project

- ✓ Proposed methods include genotoxicity, dermal irritation/sensitization, phototoxicity, and acute aquatic toxicity at a minimum

Next Steps

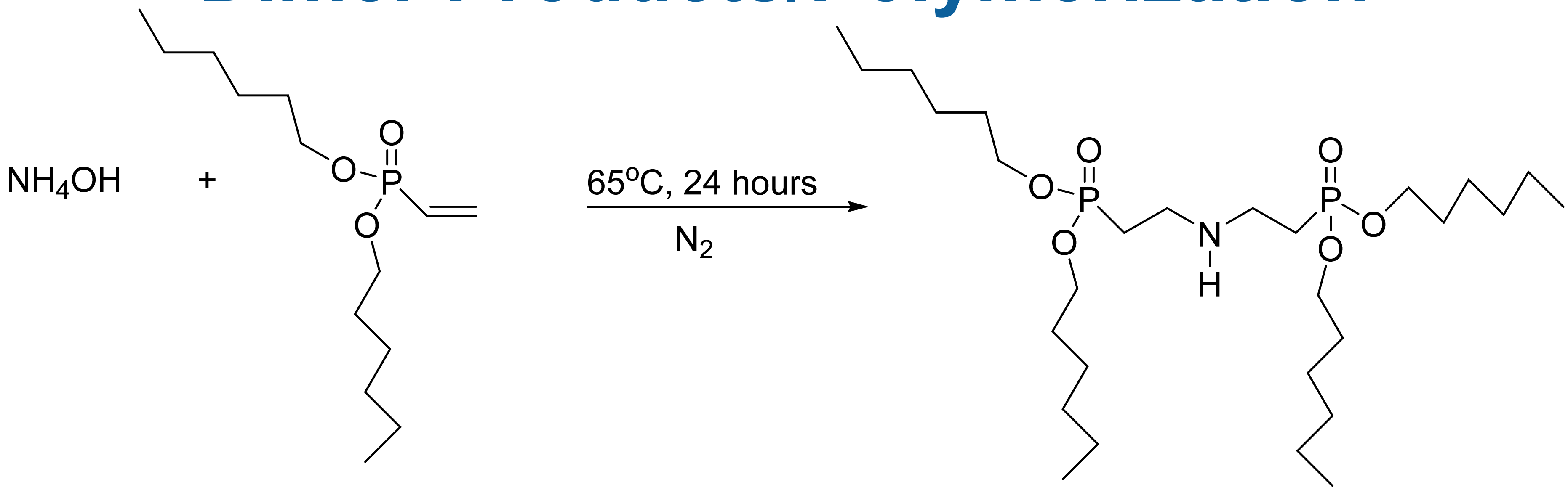
Synthesis of Dihexyl vinylphosphonate Didodecyl vinyl phosphonate



The above compounds dihexyl and didodecyl have not been prepared,
synthesis based on literature sources listed below for diethyl vinylphosphonate(commercial product/Aldrich Chemicals)

Karimov, K. R. et al., *Izvestiya Vysshikh Uchebnykh Zavendenii, Khimya I Khimicheskaya Teknologia*, **32(10)**, 34-36 (1989)
Pergament, I., et al., *Organic Letters*, **3(2)**, 217-219 (2001)

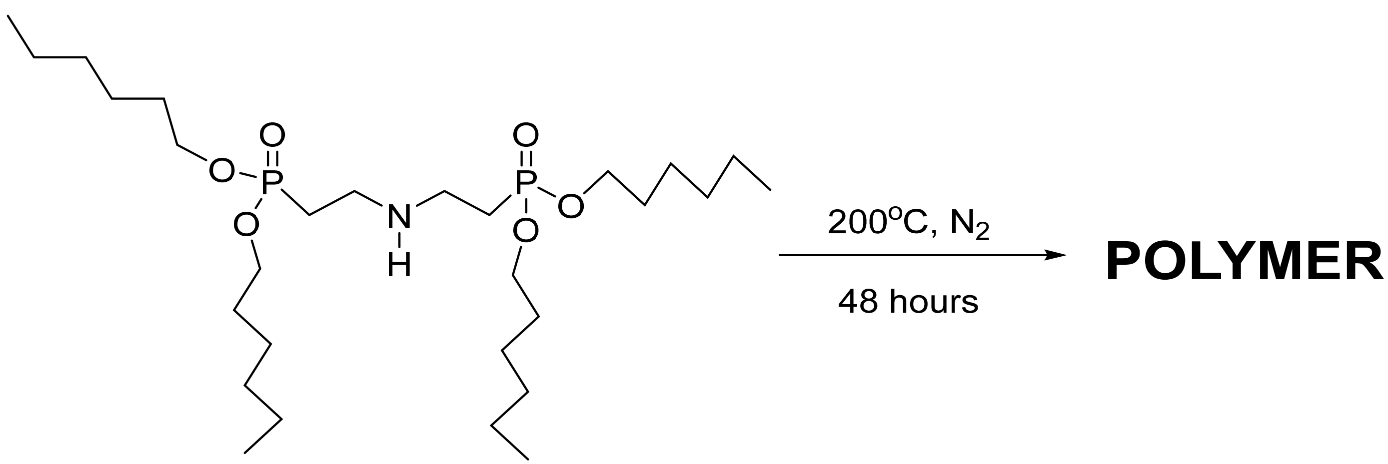
Preparation of the Dihexyl and didodecyl Dimer Products/Polymerization



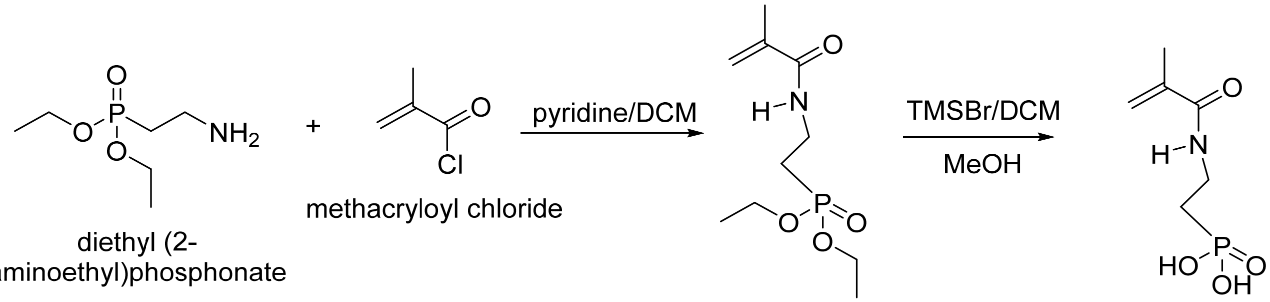
tetrahexyl (azanediylbis(ethane-2,1-diyl))bis(phosphonate)

Chemical Formula: $C_{28}H_{61}NO_6P_2$

Elemental Analysis: C, 59.03; H, 10.79; N, 2.46; O, 16.85; P, 10.87



Complete Synthesis/Characterization of Poly(n-alkyl(2-methacrylamidoethyl)phosphonate

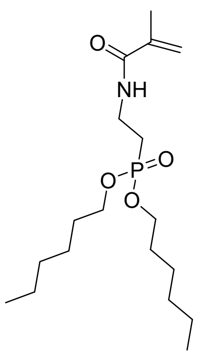


diethyl (2-aminoethyl)phosphonate

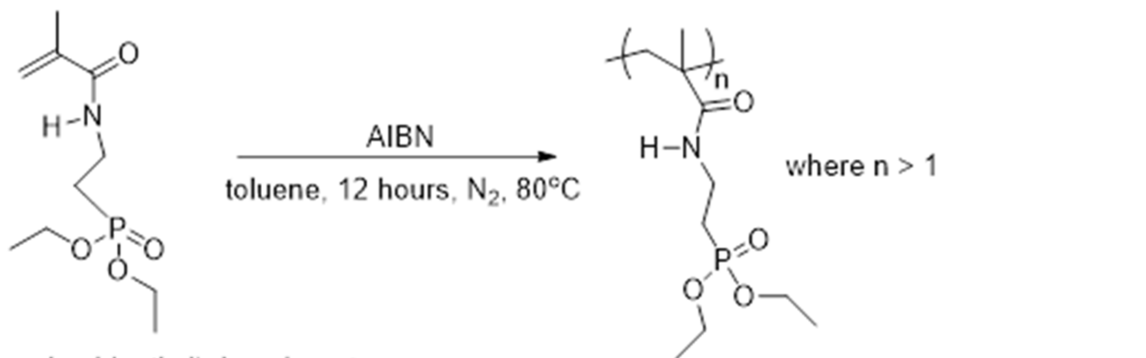
methacryloyl chloride

diethyl (2-methacrylamidoethyl)phosphonate

(2-methacrylamidoethyl)phosphonic acid

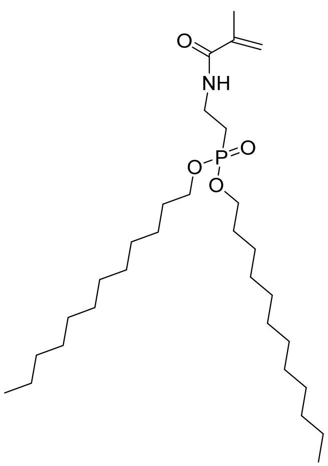


dihexyl (2-methacrylamidoethyl)phosphonate



diethyl (2-methacrylamidoethyl)phosphonate

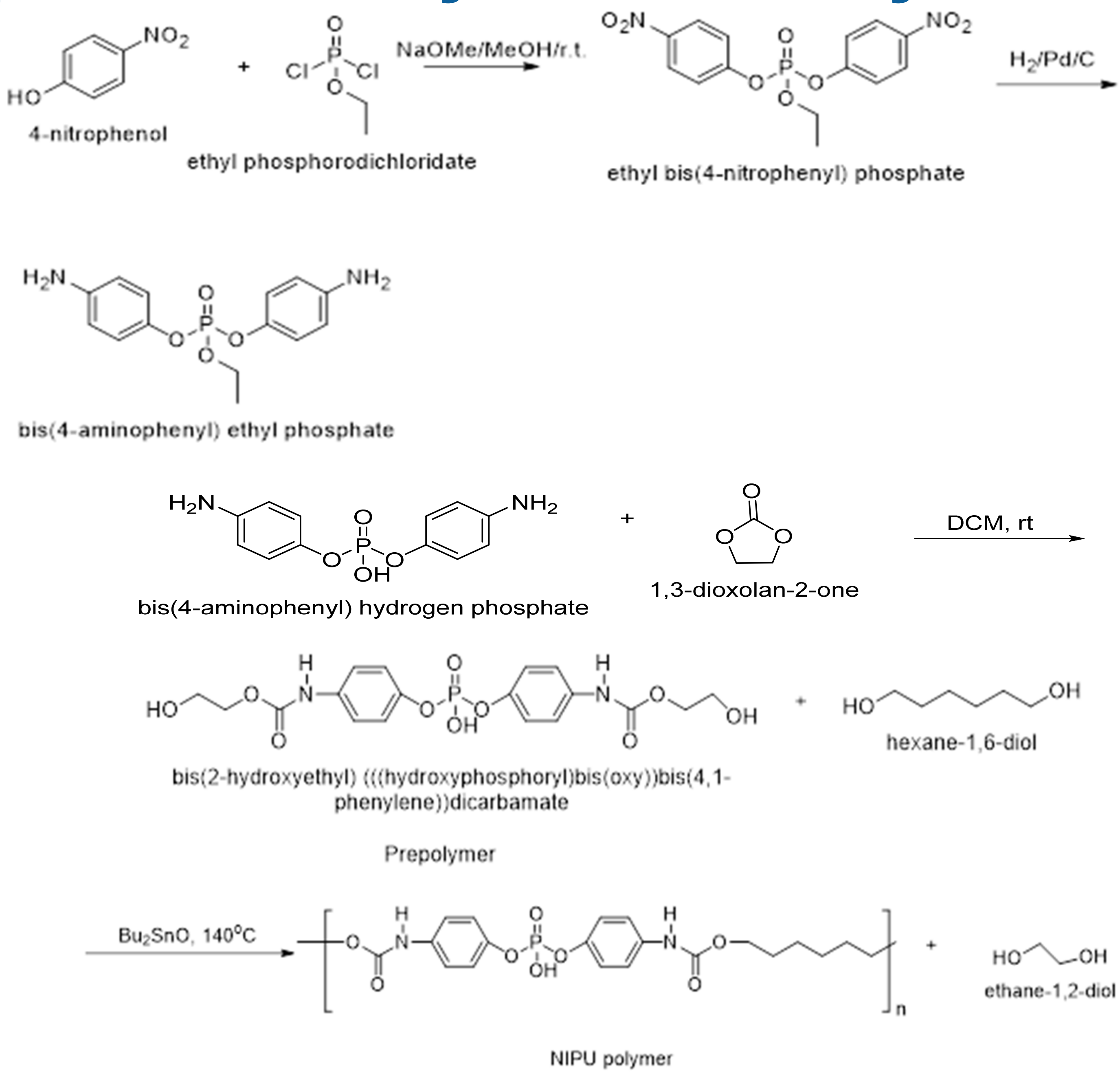
Poly(diethyl(2-methacrylamidoethyl)phosphonate))



didodecyl (2-methacrylamidoethyl)phosphonate

Co-polymers based on diethyl (hydrophilic components and hydrophobic (dihexy and/or didodecyl) via anionic and/or RATF polymerization methods

Complete NIPU Synthesis/Polymerization



Key Points

- Synthesis/Characterization of several intermediates and monomers completed
- Highly water soluble homopolymer based on Tetraethyl(azanediylbis-(ethane-2,1-diyl)bis(phosphonate) polymerized via melt
- Formulated in fluorine-free AFFF
- Poor fire suppression activity
- Need both hydrophilic and hydrophobic components to have effective fire suppressive properties (hydrophobic segments must solubilize the foam produced during spray-surfactant properties)

Future Research

- Synthesis scheme provided for innovative hydrophilic/hydrophobic polymer compounds
- Several intermediates/monomers prepared
- Key feature is the combination of the long chain n-alkyl groups to impart hydrophobicity for these compounds (surfactant based compounds)
- Static and dynamic contact angles (CA) will be measured via optical tensiometer as well as the surface tension using an inverted measurement called the “rising bubble,” which is used to measure interfacial tension between two immiscible liquids
- Formulate into fluorine-free AFFF formulations
- Test fire suppression properties of surfactants compounds

WP22-C2-3235: Environmentally benign-phosphorous polymer(s) based fire suppression additives via an intumescence mechanism

Performers: PI: Peter Zarras (NAWCWD)
Co-Performers: APHC

Technology Focus

- *Functional Additives and Foam Formation to Enhance PFAS-Free Fire Suppressants for Military Use*

Research Objectives

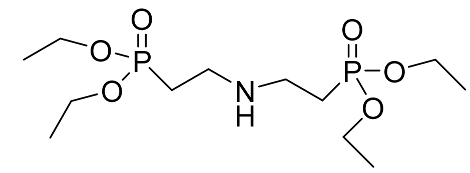
- *Synthesize/characterize innovative fluorine-free AFFF compounds for fire suppression via an intumescence fire-suppression mechanism*
- *Meet or exceed performance specification fire-extinguishing agent, aqueous film forming foam liquid concentrate for fresh and seawater MIL-PRF-24385(SH) w/int. amendments*

Project Progress and Results

- *Synthesis/characterization of innovative water soluble tetraethyl(azanediylbis-(ethane-2,1-diyl)bis(phosphonate) (Dimer product)*
- *Formulated into a fluorine-free AFFF*
- *Poor fire suppression properties displayed during testing*
- *Must impart surfactant properties to these derivatives*

Technology Transition

- *Request SEED continuation funds FY24: ($250K) to determine conclusively whether the hypothesis "an intumescence fire-suppression mechanism" can be achieved with our system meeting the fire-extinguishing requirements found in MIL-PRF-24385(SH) w/int. amendments*



tetraethyl(azanediylbis-(ethane-2,1-diyl) bis(phosphonate) (Dimer product)

Failure at suppressing fire during 60 second test