Isocyanate-Free Solid Rocket Motor Propellant Binders Inspired by Nature

Project Number (WP-2406)

Dr. Andrew J. Guenthner
Lead, Applied Materials Group, Propellants Branch
Air Force Research Laboratory, Aerospace Systems Directorate
Edwards AFB, CA 93524

Brief to SERDP
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SERDP
DOD ▪ EPA ▪ DOE

Performers

Mr. Jacob Marcischak

AFRL Propellants Branch Applied Materials Group

Gumstock & Inert Production / Characterization

Dr. Timothy Haddad, Dr. Josiah Reams, Mr. Michael Ford

ERC Incorporated (AFRL Propellants Branch)

Chemical Synthesis, Ageing Studies

Dr. Michael Kramer, Mr. Paul Jones

AFRL Propellants Branch, Propellant Manufacturing Group

Production of Propellants

Problem Statement

- The predominant cure chemistry for solid propellants (and many explosives) requires small-molecule isocynates. These compounds are a significant occupational health hazard, with effects including occupational asthma and cross-sensitization to other irritants. The use of isocyanates in the workplace is becoming increasingly difficult and expensive to support. The life cycle of DoD solid propellant ingredients spans many decades. An affordable and sustainable isocyanate replacement chemistry will need to avoid significant environmental safety and occupational health issues over its entire life cycle, which could be well into the 22nd century. Curative systems based on ubiquitous, naturally-occurring chemistries, if developed successfully, will mitigate the existing occupational health issues associated with isocyanates, as well as provide the best possible hedge against potential future issues.

Technical Objective

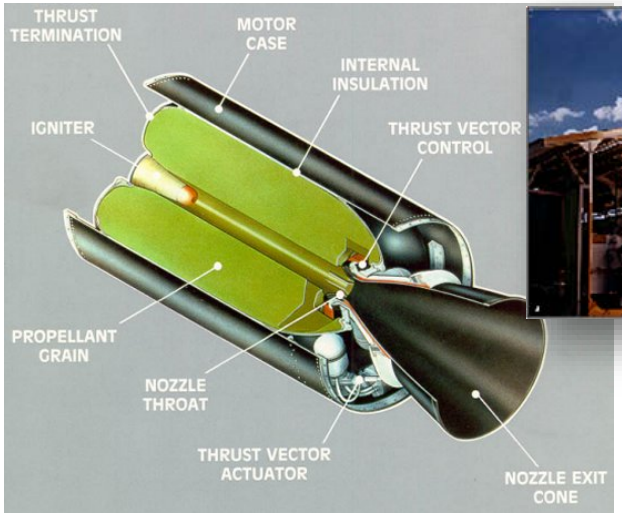
- Mitigate the technical risk associated with developing propellant curatives based on naturally-occurring chemistries through identification and exploration of promising candidates for the replacement of isocyanates.

Background/Previous Work Outline

- Introduction to Solid Propellant Cure
- Nucleobase Binding
  - Comparison with Chemical Cross-linking
- Sulfur-Based Cure Chemistry
  - Previous Use in Propellants (Disulfides)
  - Thiol-ene Chemistry
- Health, Safety, and Environmental Issues

Solid Propellant Cure

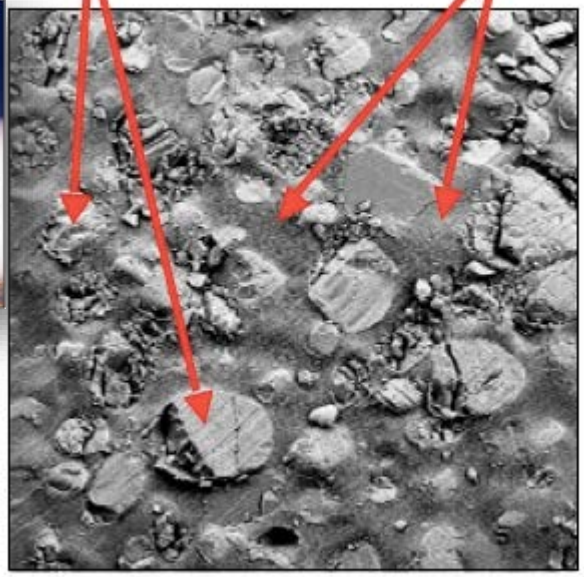
- Composite solid propellants are highly filled elastomers; the solid filler particles are mixed thoroughly with a liquid “prepolymer”, which solidifies via chemical reaction
- The reactions must take place at a fairly low temperature to maintain safety
- The reaction rate must be slow enough to allow for complete mixing (8 hours) but fast enough to make mechanically viable castings within about 14 days
- The most desirable reactions are controlled via catalysts but not affected by other ingredients



Solid rocket motor

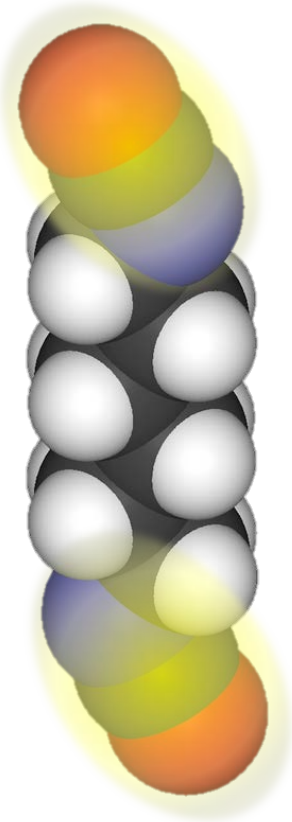
Fuel and.or oxidizer particles

“Binder”



Micrograph of solid propellant

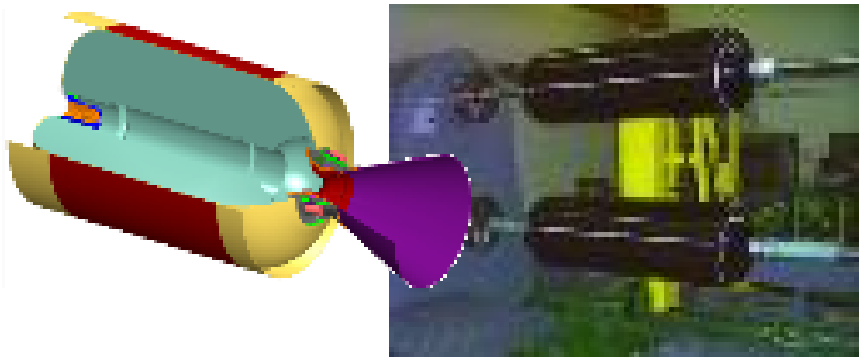
SOTA Curative: Isocyanates



- Production was roughly 4 billion kg in 2000
- Isocyanates are prized for their high reactivity; they are particularly useful for production of energetic materials where high temperatures must be avoided
- Isocyanates are a respiratory irritant and a significant cause of occupational asthma
- Sensitization can occur at very low levels of exposure, with effects continuing for many years afterward
- Cross-sensitization (e.g. dermal exposure leading to sensitization of respiratory tract) has also been reported.
- Isocyanates are not found in nature; their high reactivity without specificity makes them unsuitable for complex biological systems

Desired Characteristics of Isocyanate Replacements

- Significantly reduce occupational safety and health issues
- Maintain propellant performance characteristics (specific impulse, burn rates, ageing)
- Compatible with existing manufacturing processes
- Useful in a wide variety of formulations (strategic, tactical low & min smoke, warhead explosives, etc.)



Replacements need to have minimal chance of discovery of as yet unknown environmental, safety, and occupational health issues

Approach: Use Ubiquitous Chemistry Found in Nature

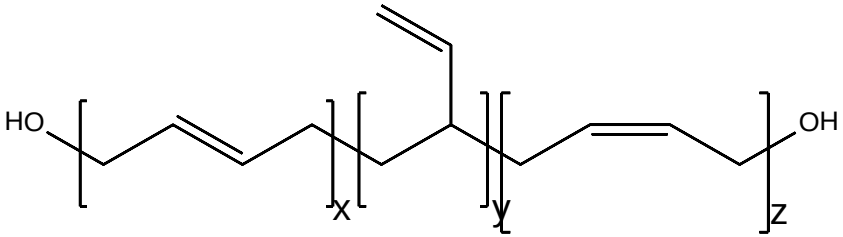
- Least likely to face increased regulation in the future
- Matches trends in industry, but none currently suitable for propellant development
- Allows for many options -- three chosen to maximize chance of success with available resources

Approaches Selected

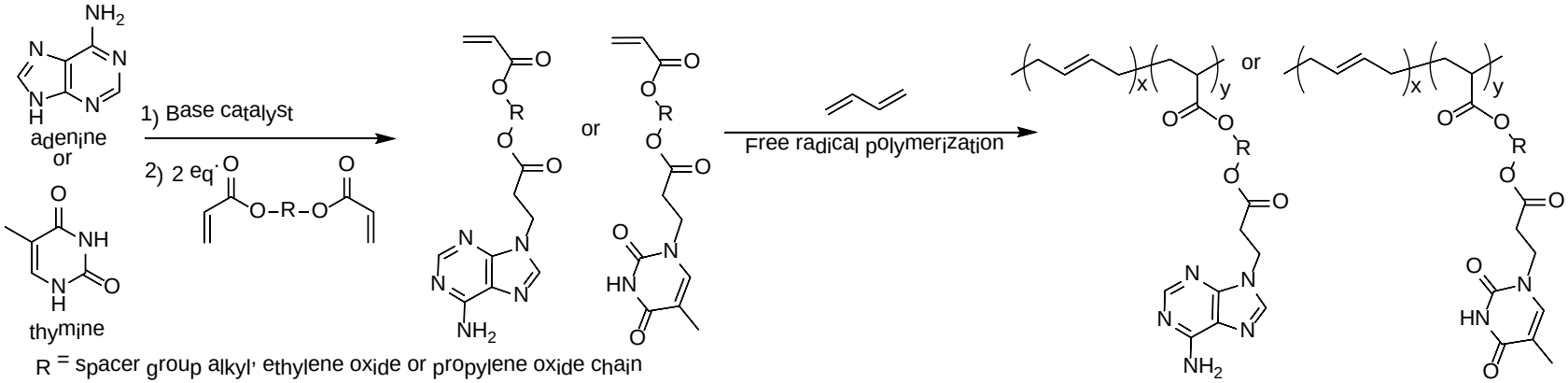
- Nucleobase Binding – how DNA is held together
- Sulfide-based Cross-linking – how hair and hard proteins (e.g. claws, nails) are made strong
- Reactivity of Natural Oils – uses common processes found in fats, oils, and greases, successful commercialization record
- Prepolymers will incorporate these alternative cure approaches while retaining chemical similarity to existing binder prepolymers

Synthesis of Nucleobase Polymers

Replace the state of the art prepolymer hydroxyl-terminated polybutadiene (HTPB) …

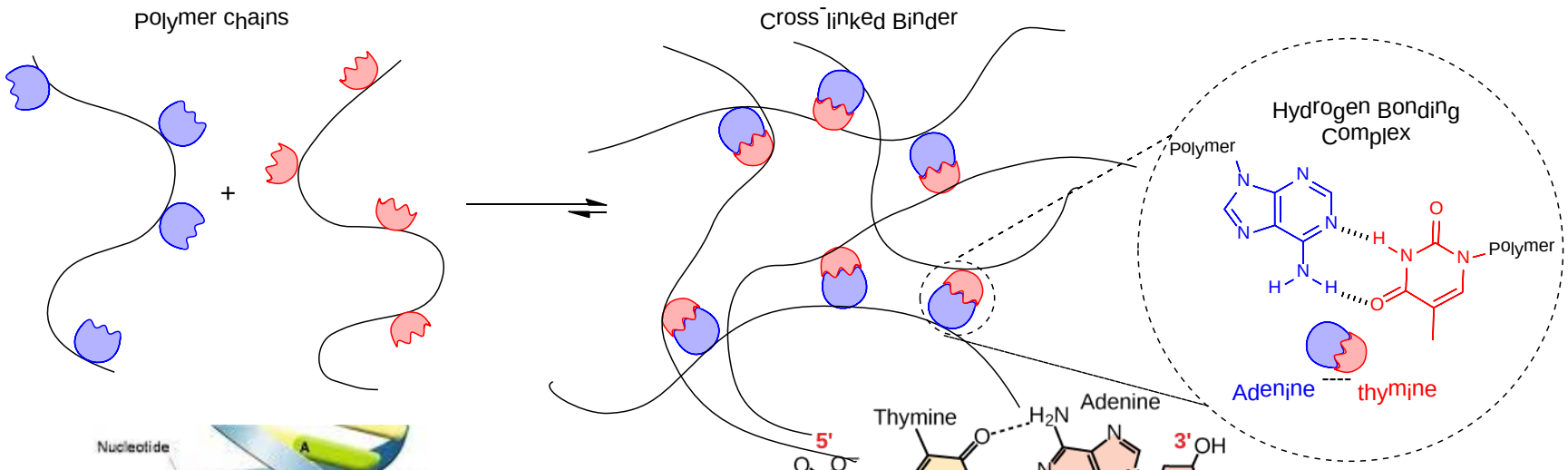


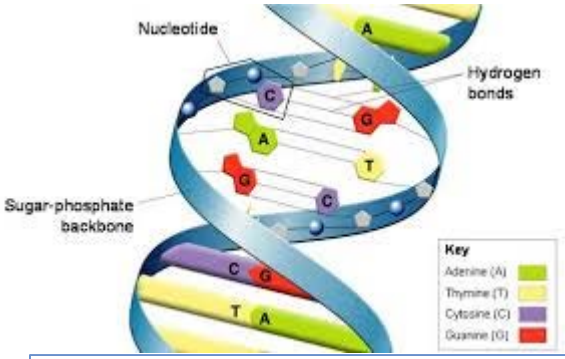
With a nucleobase-containing polybutadiene



Two-step synthesis produces an “HTPB-like” polymer prepolymer that incorporates adenine and thymine side groups. These groups are randomly distributed along the polymer chain.

Nucleobase Polymer Concept



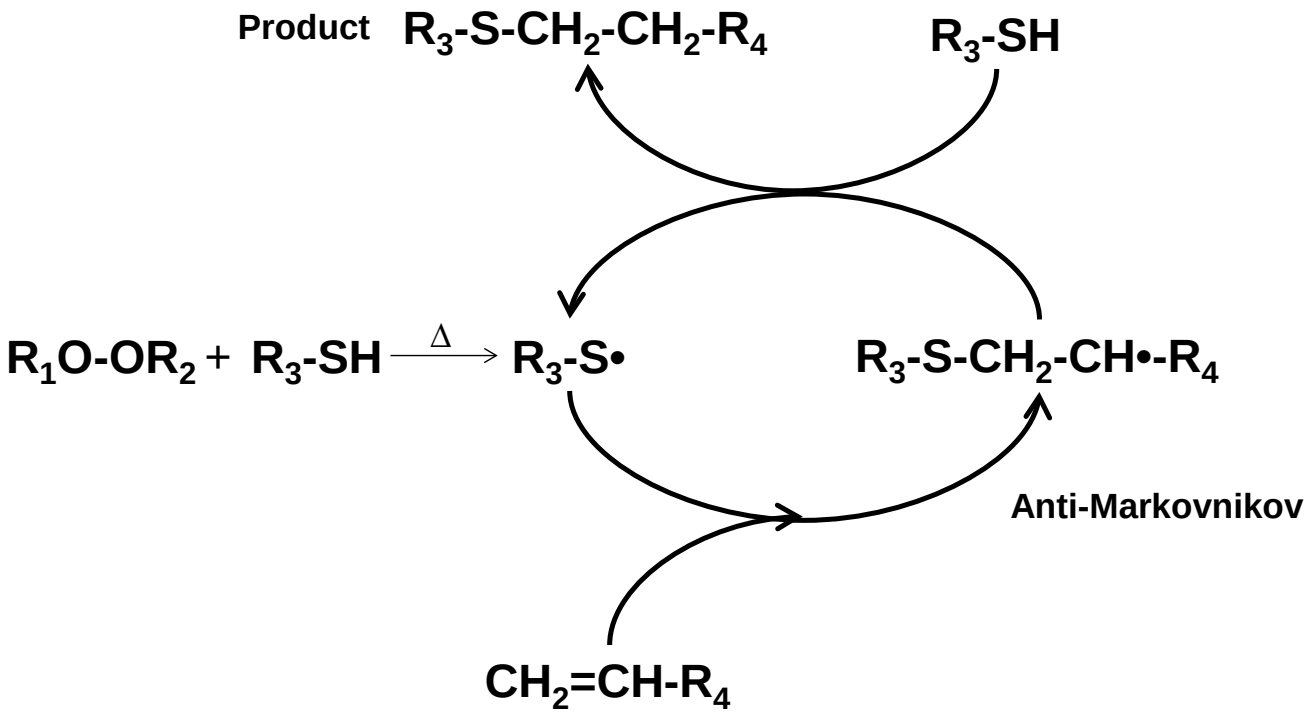


The adenine and thymine groups have limited affinity for binding with themselves, but strongly bind to one another, just as in DNA. This binding represents an effective substitute for cross-linking. Nucleobase binding for non-polar hydrocarbon prepolymers has never been done previously.

Use of Disulfides in Propellants

- Elemental sulfur used in gunpowder since 13th century (free radical cross-linking)
- Many early solid propellant formulations from the 1940s-70s relied on disulfide/polysulfide cure of elastomers
- Disulfides (C-S-S-C) contain a S-S bond, which is much less thermally stable than a C-S bond (sulfide, C-S-C).
- In the early 1970s, the reaction of thiols (C-S-H) with vinyl groups (C=C-H) to form sulfides was investigated. Because the reaction mechanism was unknown, appropriate cure conditions and proper control of the reaction were never achieved.
- Sulfur-based cure chemistry could be utilized with 1) existing vinyl groups on HTPB, 2) vinyl-functional prepolymers, 3) vinyl-functional curatives w/ thiol-terminated prepolymers, and 4) natural oil curatives

Thiol-Ene Chemistry



The controlled radical chemistry of thiol-enes produces a well-defined “click” reaction to link molecules together, in contrast to the variable products formed by uncontrolled radical cross-linking. The nature of the thiol-ene reaction was not understood prior to the 1980s, and not widely known prior to the 2000s.

Environmental, Safety, and Occupational Health Issues

- Nucleobase Prepolymers
  - Nucleobase functionality ubiquitous in nature, in similar polymer-attached form to proposed use, ingested by animals in large quantities, low water solubility limits contamination threat.
  - “Might attract bugs” is main issue
- Sulfur-based chemistry
  - Thiols and disulfides ubiquitous in nature, ingested by animals in large quantities (e.g. eggs), sulfides also found in proteins
  - Thiol-ene curatives are typically considered safe for use in biological systems as medical and dental implants, but limited experience base exists
  - Natural oils are also ubiquitous and ingested by animals in large quantites
  - Disulfides prone to breakdown, but aliphatic sulfides should be inert and stable, oxidized forms (sulfoxides / sulfones) even more stable

Results Outline

- Overall Risk Reduction Achieved
- Nucleobase Binding
  - Synthesis (Task 1)
  - Cross-linking (Task 2)
- Sulfur-Containing Chemistry
  - Synthesis (Task 1)
  - Cross-linking (Task 2)
- Inert Formulation and Testing (Task 3)
- Propellant Formulation and Testing (Task 4)
- Extended-SEED Results

Abridged Risk Reduction Matrix (1/3)

Risk	Likelihood / Consequences	Level of mitigation achieved for …				
		Nucleo-base Polymer	Thiol-ene Cured HTPB	Thiol-term. HTPB	Thiol-term HLBH	Vinyl ether-term HLBH
Prepolymer molecular weight outside of target range	Moderately likely; severe consequences	Fair	Good	Poor	Fair	Good
Prepolymer functional group yield outside of target range	Likely; severe consequences;	Fair	Good	Poor	Good	Good
Prepolymer thermo-physical characteristics incorrect	Moderately likely; severe consequences	Good	Good	Fair	Good	Good
Cure time/temperature profile and control does not match SOTA propellant requirements	Moderately likely; severe consequences;	Poor	Good	X	Good	Good

Only risks with a “fair” or “poor” outcome are shown

Abridged Risk Reduction Matrix (2/3)

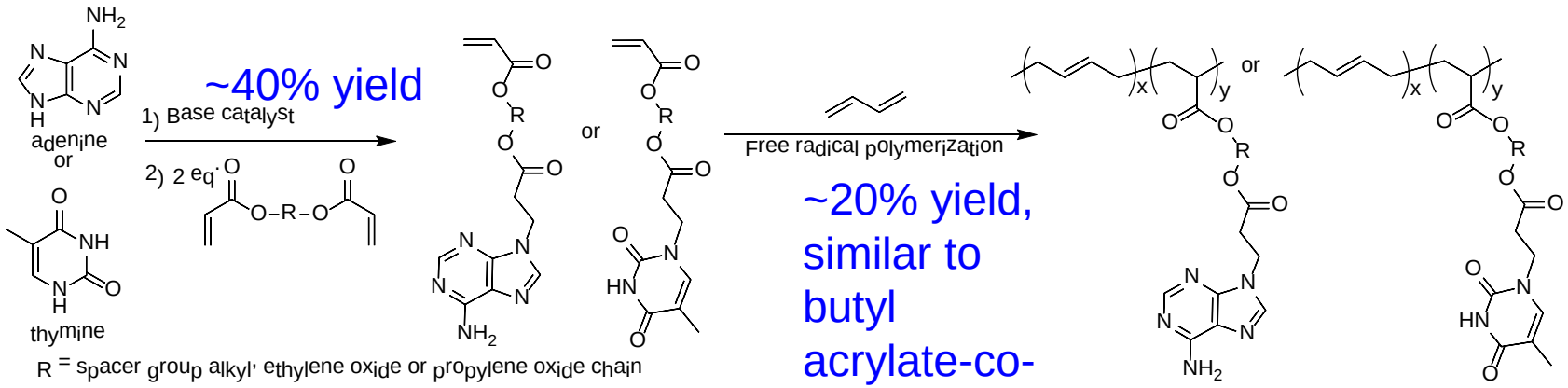
Risk	Likelihood / Consequences	Level of mitigation achieved for …				
		Nucleo-base Polymer	Thiol-ene Cured HTPB	Thiol-term. HTPB	Thiol-term HLBH	Vinyl ether-term HLBH
Non-ideal network formation	Low to moderate likelihood; moderate to severe consequences	Poor	Good	X	Good	Good
Gumstock thermal stability too low	Low likelihood (if prepolymer risk mitigated); moderate to severe consequence	X	Good	X	Fair	Good
Inert formulation mechanical properties unacceptable	Moderate to high likelihood; severe consequence	X	Poor	X	X	Good

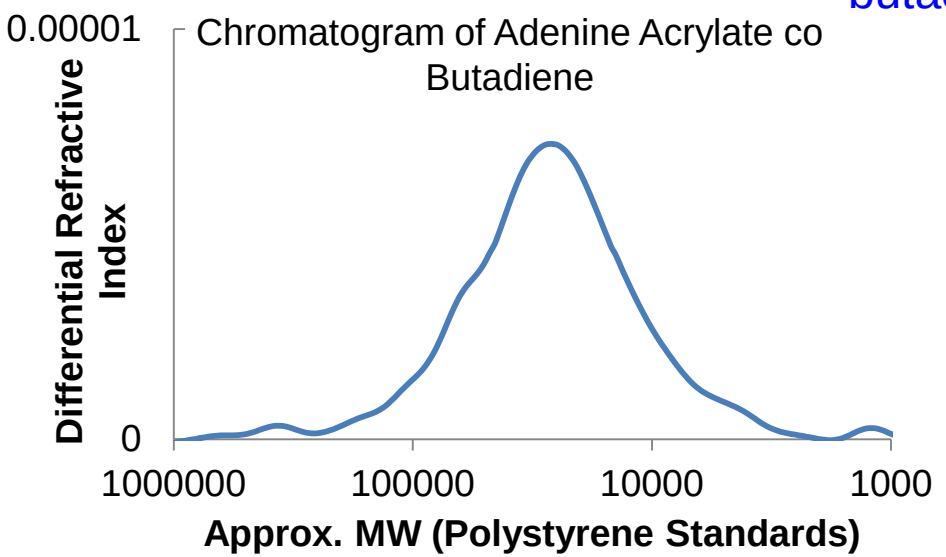
Abridged Risk Reduction Matrix (3/3)

Risk	Likelihood / Consequences	Level of mitigation achieved for …				
		Nucleo-base Polymer	Thiol-ene Cured HTPB	Thiol-term. HTPB	Thiol-term HLBH	Vinyl ether-term HLBH
Burning rate outside of acceptable range	Low likelihood (if prepolymer risks mitigated); moderate consequences	X	X	X	Fair	✓ Fair
Ageing rates too rapid or uncertain	Low to moderate likelihood; severe consequence	X	X	X	Fair	✓ Fair
Propellant manufacturing issues that preclude development	Moderately likely; moderate to severe consequence	X	X	X	Fair	Good
Propellant characteristics that preclude development	Low to moderate likelihood; moderate to severe consequences	X	X	X	Fair	Good

Achieved "Good" rating after extended SEED

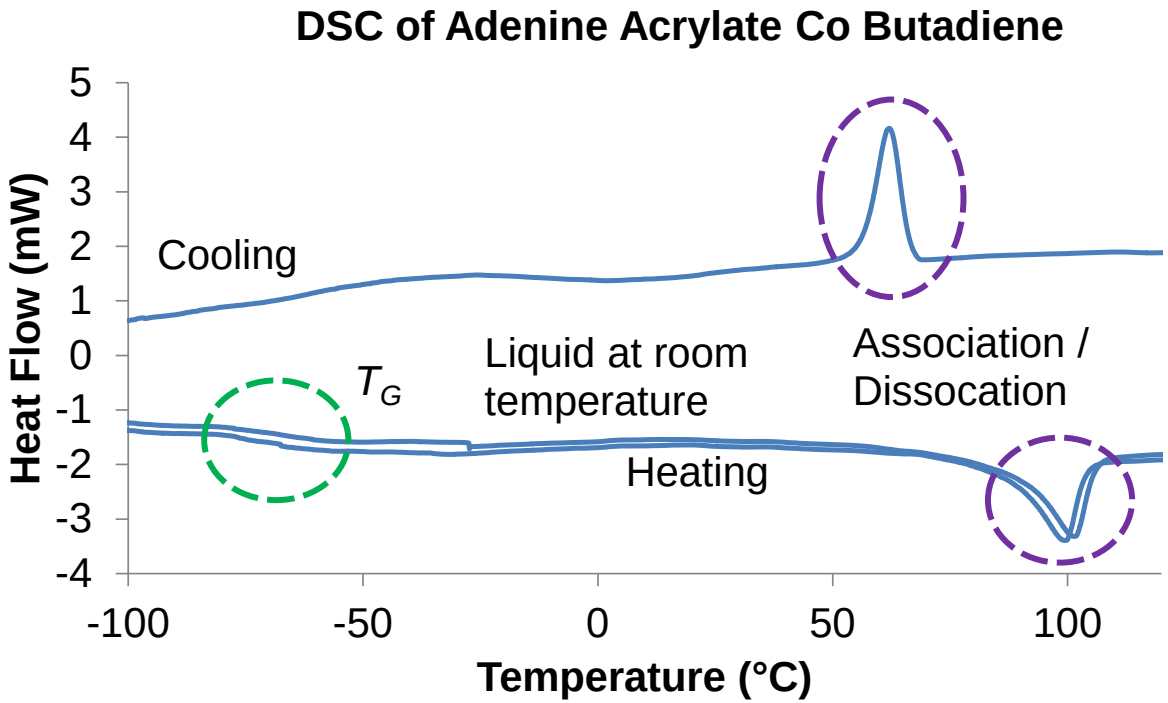
Synthesis of Nucleobase Polymers





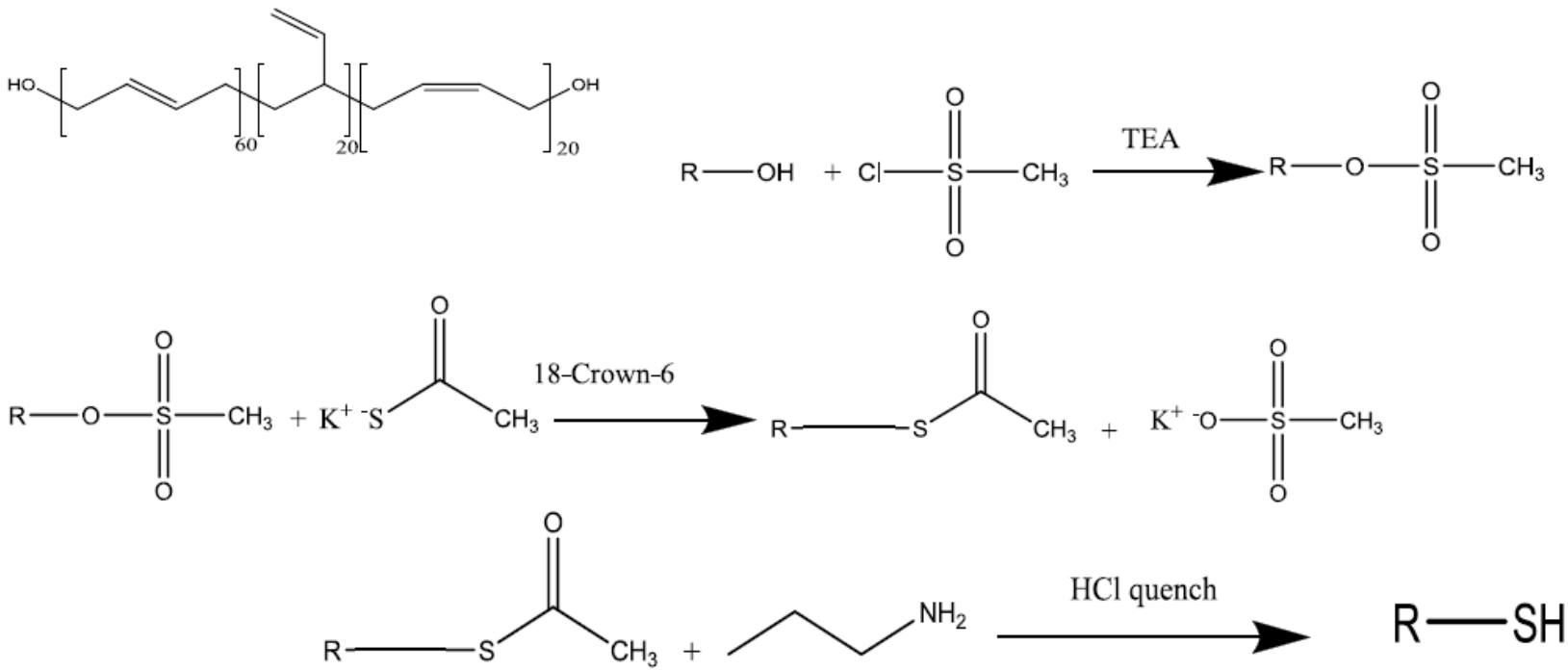
Both adenine and thymine acrylate-co-butadiene polymers were synthesized successfully. Thymine content was well-controlled, but adenine content was somewhat variable.

Binding of Nucleobase Polymers



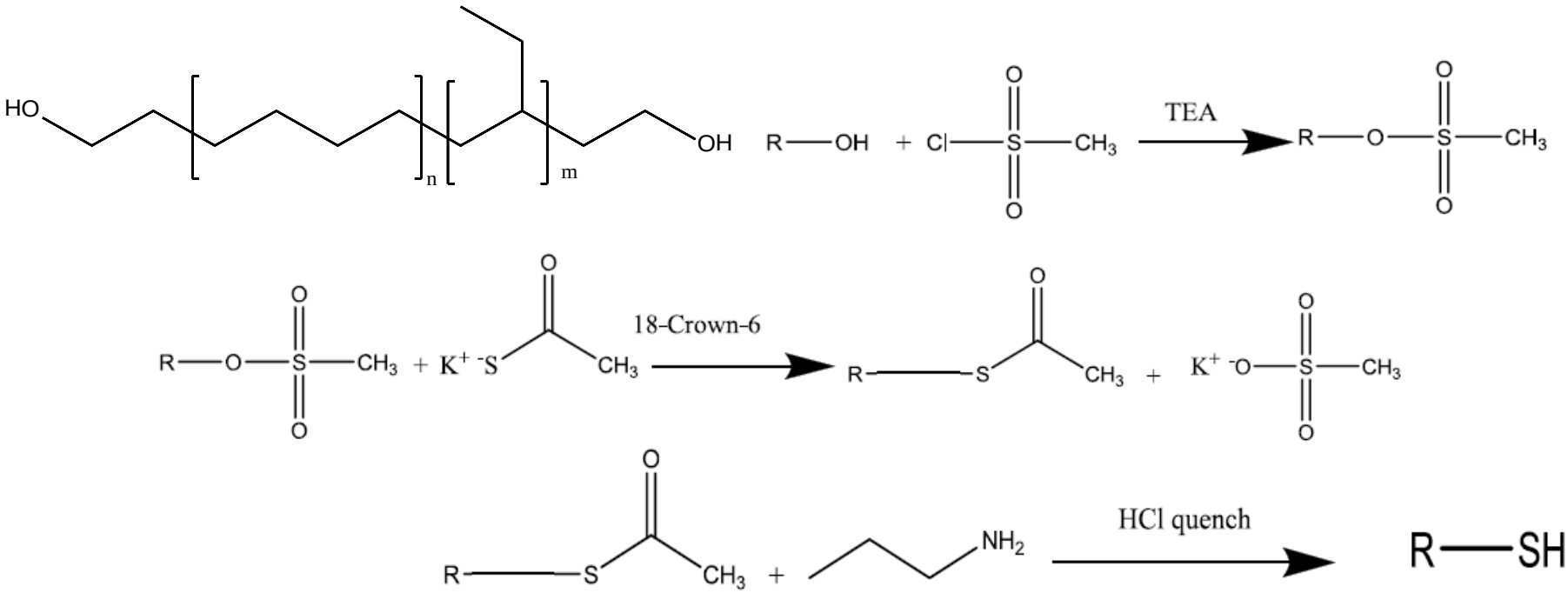
Although the thymine-containing polymer showed no self-association, the adenine-containing polymer showed significant self-association, making it difficult to mix with the thymine-containing polymer under process-appropriate conditions. Because polybutadienes are significantly more hydrophobic than previously-prepared adenine-containing polymers, the self-associating character was enhanced.

Synthesis of Thiol-Terminated Polybutadiene



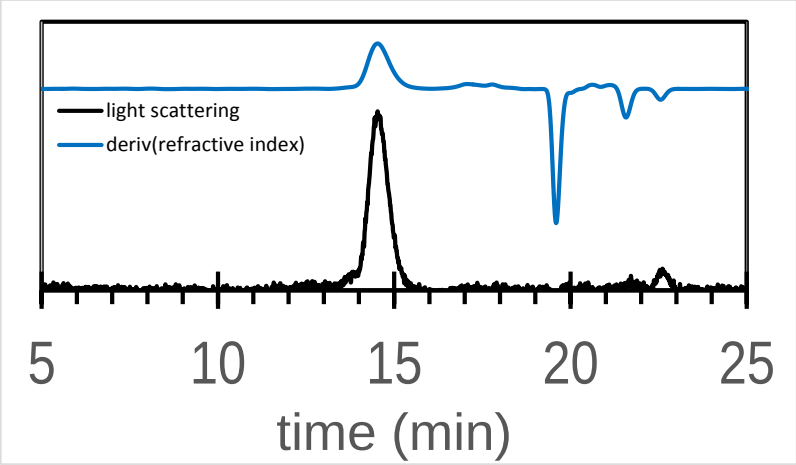
Synthesis proved daunting because of differing reactivity of terminal –OH groups in HTPB, making it difficult to achieve completion while avoiding side products.

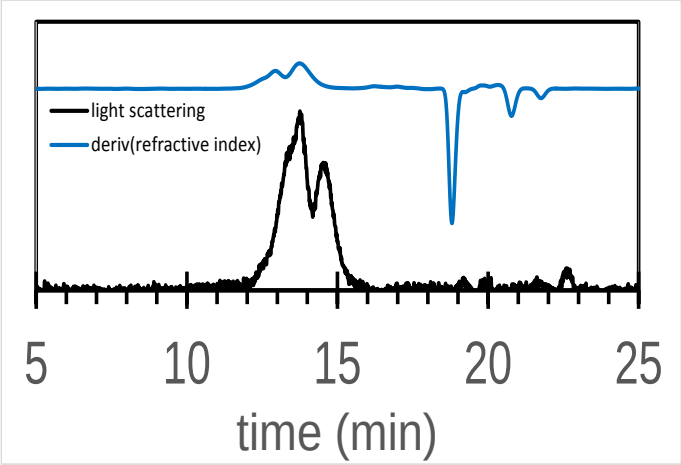
Synthesis of Thiol-Terminated Hydrogenated Polybutadiene



The –OH end group reactivity is much less variable, allowing for synthesis to proceed in good yield for the first two steps, and with moderate yield for step 3.

Molecular Weight of Thiol-Terminated Hydrogenated Polybutadiene



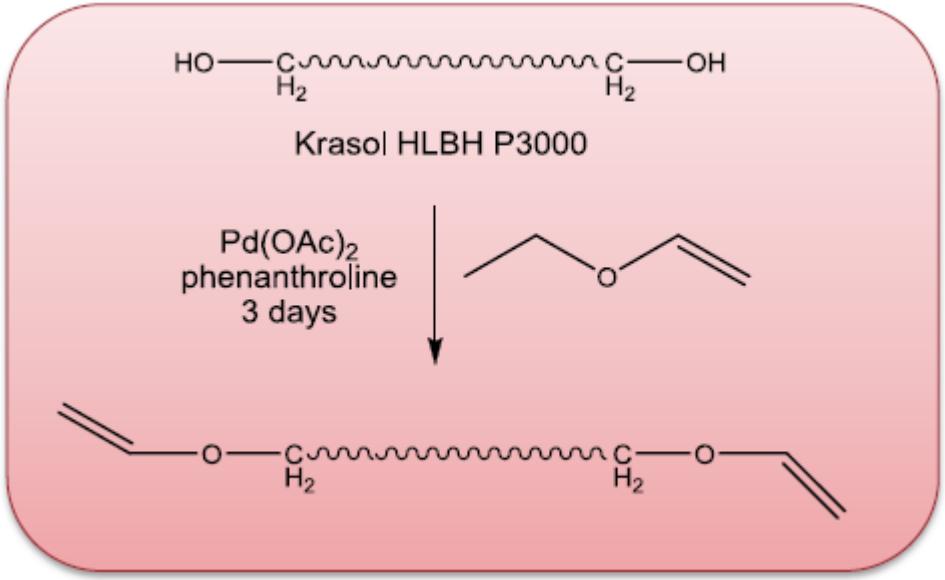


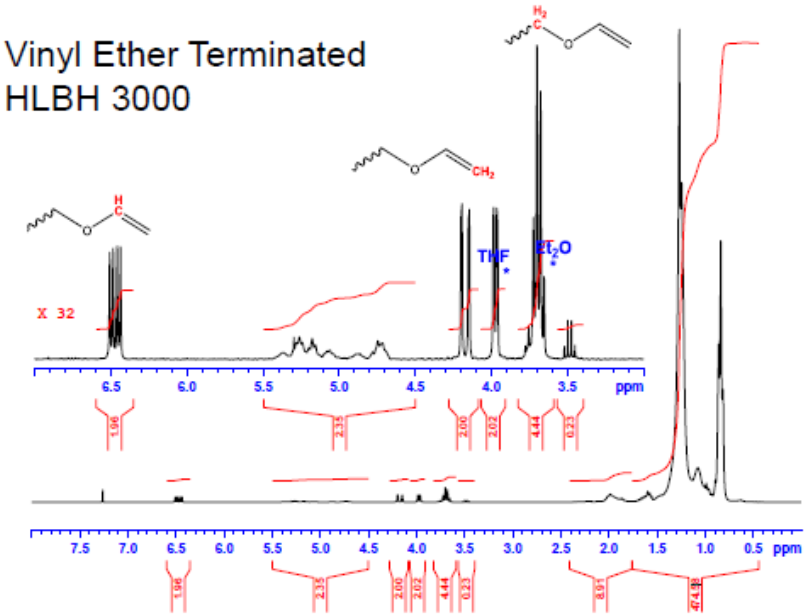
Starting material: HLBH 3000 (-OH terminal hydrogenated polybutadiene)

Two peaks, one for polymer with same MW as starting material (expected), one for higher MW polymer (linked by S-S bonds)

Size exclusion chromatography (shown above) shows clearly that some polymer chains become longer. Using nuclear magnetic resonance, in the best case, about 25% of the terminal –SH groups are converted to disulfide bonds.

Vinyl Ether-Terminated Hydrogenated Polybutadiene





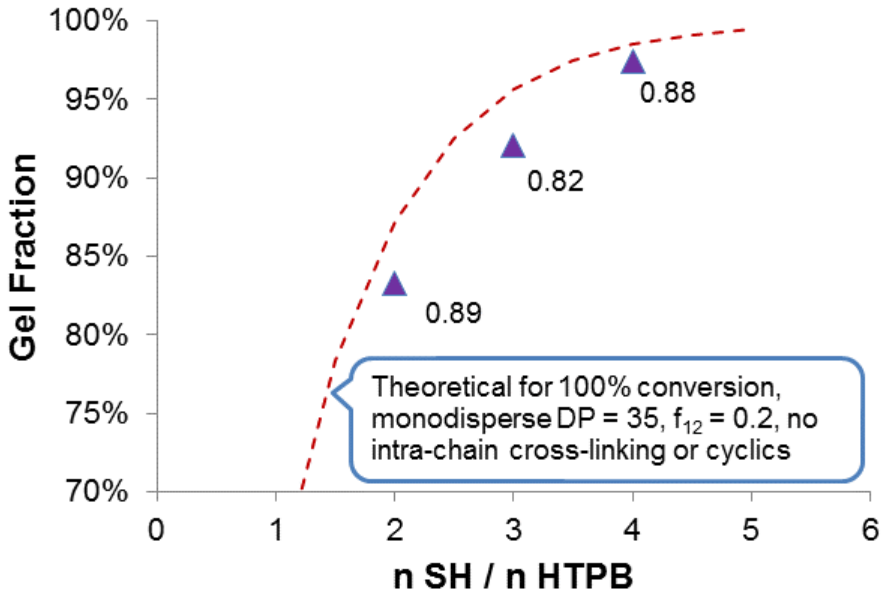
Only by-product is ethanol

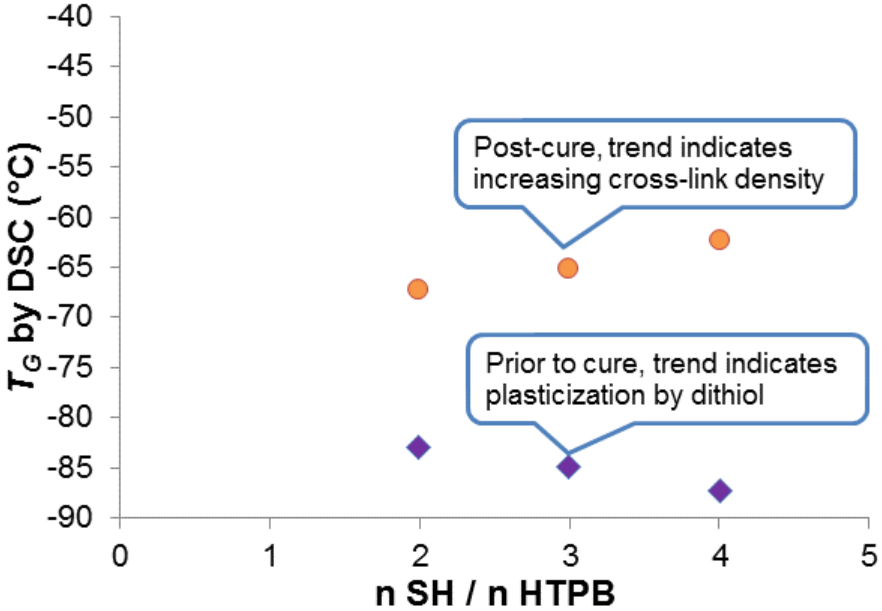
Modification proceeds in nearly quantitative yield in one step. Inductively-coupled plasma mass spectroscopy shows that residual Pd levels are < 5 ppb

Summary of Results from Sulfur-Containing Systems

- HTPB cross-linked directly with thiols
  - Leads to networks with low strain to failure
- Polybutadiene (PB) with low vinyl incorporation
  - Leads to networks with low strength
- Thiol-terminated polyethylene glycol (PEG) system
  - Suitable vinyl curatives are not miscible
- Thiol-terminated polybutadiene
  - Thiol substitution reaction exhibits poor yield, many side products
  - Differences in HTPB –OH group reactivity play a key role
- Thiol-terminated Hydrogenated HTPB (HLBH)
  - Much easier to synthesize; only side reaction is some S-S formation
  - Appreciable self-reaction leads to limited pot life
- Vinyl ether-terminated polybutadiene
  - Single step reaction, much easier to scale up
  - Reaction fails for unknown reason
- Vinyl ether-terminated HLBH (VETHPB)
  - Near quantitative conversion in high yield, 1 step to stable product
  - Leads to strong elastomeric networks with high strain to failure

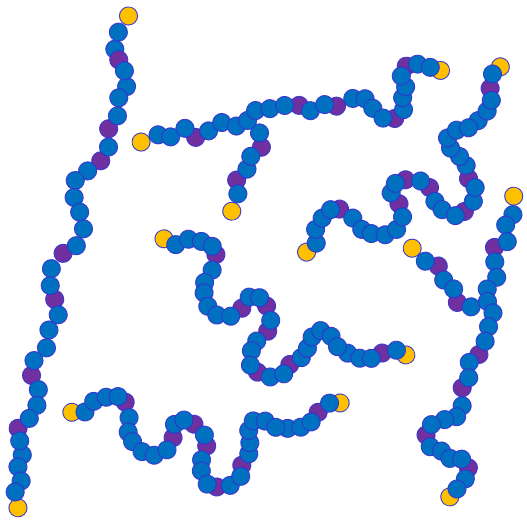
Verification of Ideal Network Formation





Work with direct cross-linking of HTPB (in which the number of cross-link junctions is high enough to permit high-quality analysis) shows that the cross-linking chemistry leads to ideal networks with low glass transition temperatures, as expected.

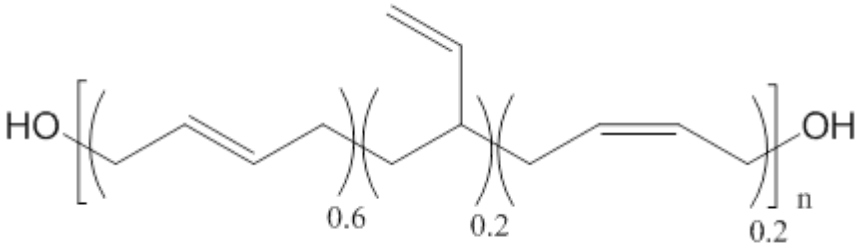
Importance of Prepolymer Architecture



Chain backbone (1,4 addition)

Vinyl goups (1,2 addition)

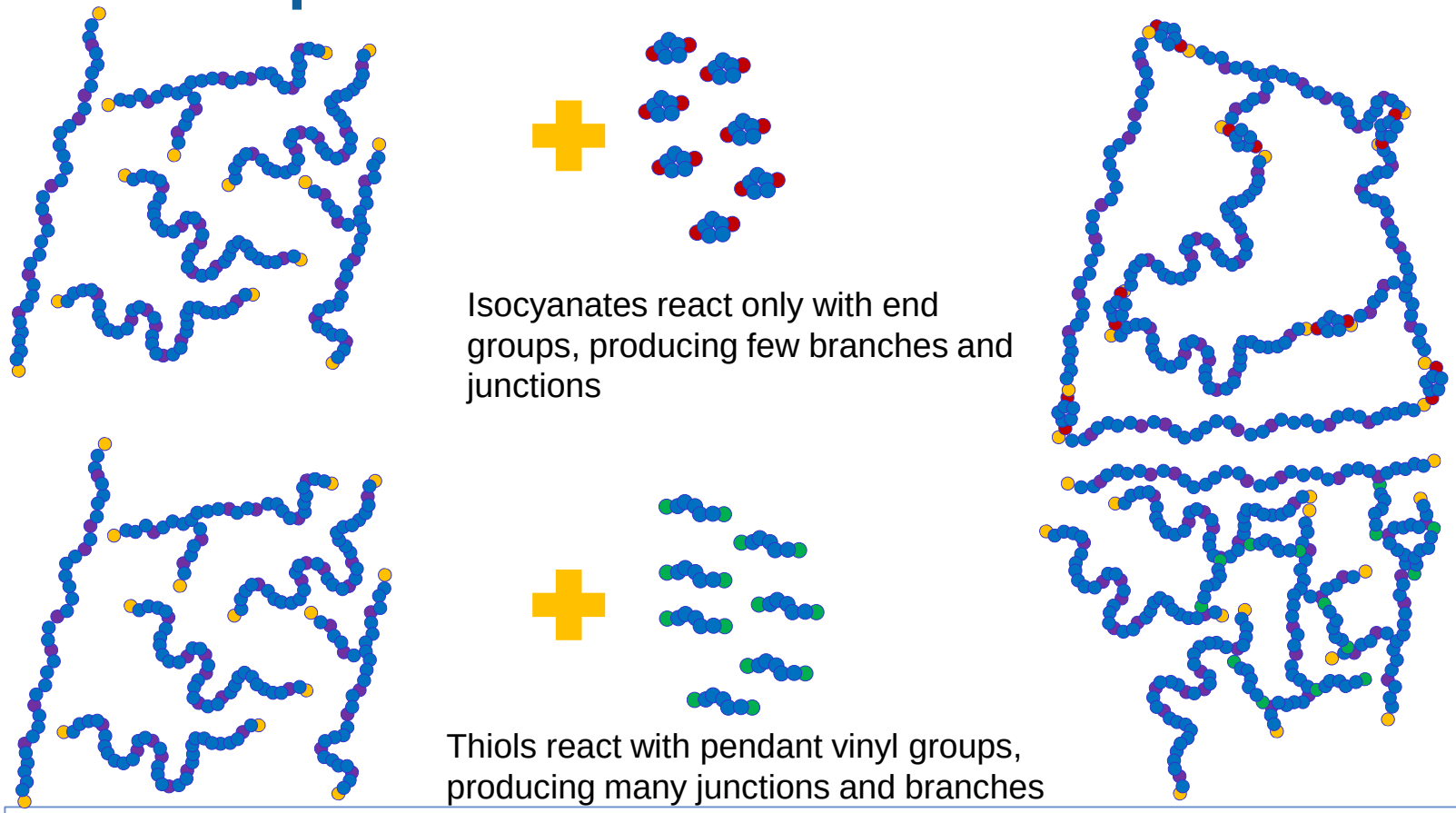
Hydroxyl end groups



- Free radical polymerized HTPB
  - Mixture of 1,4 and 1,2 addition
  - Hydroxyl end-group functionality 2.4-2.6 / per chain
  - T_g -75 ° C
  - Molecular Weight M_n = 2800 g/mol
  - Polydispersity ~2.5

In order to be used in current processes, the initial prepolymer needs to resemble current products such as HTPB at both physical and chemical levels. All sulfur-containing candidates met these criteria.

Importance of Network Architecture



In order to achieve acceptable mechanical properties, the cross-linked network architecture must also match that of HTPB. The vinyl ether-terminated HLBH matches when cross-linked with di- and tetra-thiols, while directly cross-linked HTPB does not.

Down-select Criteria

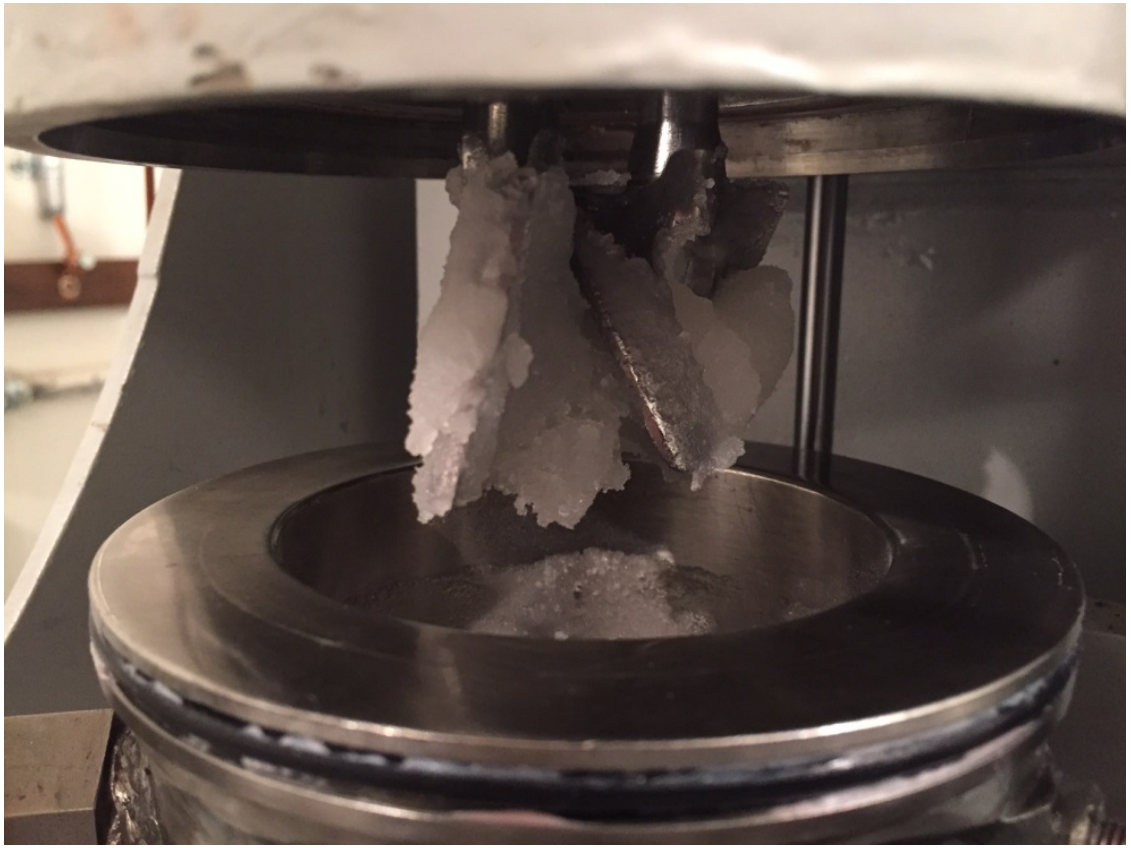
Criteria	Threshold	Thiol-HTPB	Thiol-VETHPB
Cured Tg	< -40 °C	< -61 °C	< -52 °C
5% wt loss T	>249 °C	>363 °C	>316 °C
Modulus @ 25 °C	>100 psi	140-500 psi	105 psi
Strength @ 25 °C	> 100 psi	< 50 psi	~ 100 psi
Salt Loading	>80 wt%	>80 wt%	>85 wt%
Castability	Castable after complete mixing	Castable at 8 hrs	Filled system castable after complete mixing

The vinyl ether-terminated hydrogenated polybutadiene system, cross-linked by a mixture of 1,9-nonanedithiol and pentaerythrityl tetrathiol, met all established down-select criteria for binders.

Inert Mix Testing

Process used closely mimics current inert mix testing at AFRL; solids loading kept somewhat below 80 wt% in order to avoid damage to equipment. ¼ pint scale mixer was utilized. No bubbles or other defects were observed in the cast product.

Energetic Mix Testing



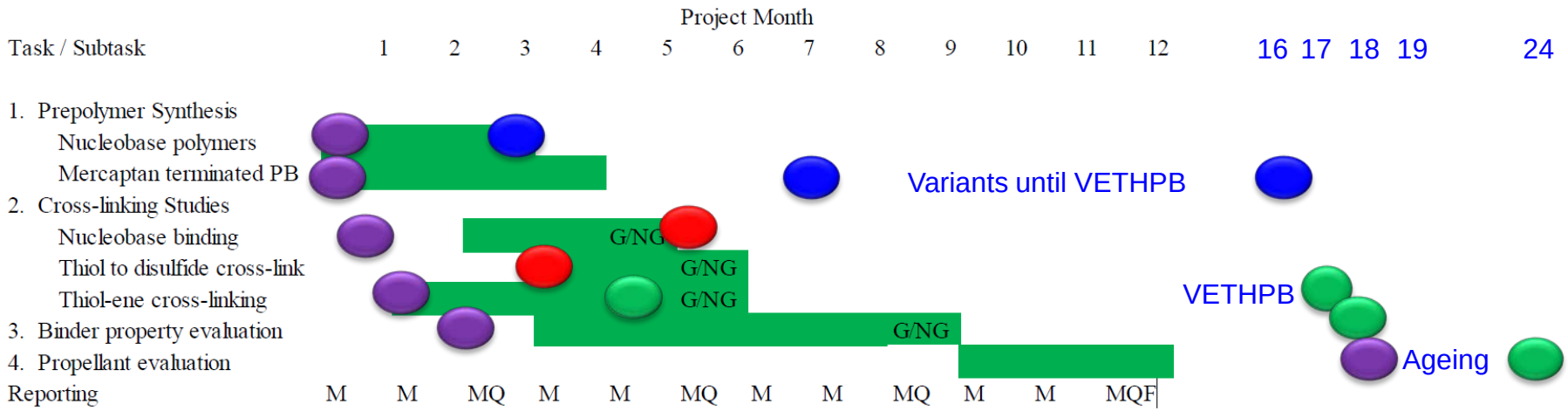
Mixes with more than 80wt% particle loading were tested at ¼ pint scale. No discoloration of AP, no bubbles or voids, and no odors associated with thiol use were noted.

Budget Review

• Budgeted Contribution from SERDP	150K
• Expended (from SERDP)	150K
• Estimated AFRL Contribution (SEED Period)	200K
• Estimated AFRL Contribution (Extended-SEED)	100K

Original proposal called for AFRL to contribute $120k. Delays in finding a suitable binder candidate for cross-linking, along with desire for extended-SEED at AFRL expense, increased AFRL contribution.

Schedule Review



Rectangles represent schedule as published in proposal; ovals represent actual completion: purple = start; blue = complete; red = no go; green = go

Deliverables Review

Proposed Deliverable	Delivered?	Comment
Nucleobase polymers at ~5 g scale	Yes, on time	Nucleobase polybutadienes now routinely available
Thiol-terminated polymers at ~5 g scale	Yes, +8 mos	HLBH version routinely available
Nucleobase candidate go / no-go	Yes, on time	No go due to self-association (not easily fixed)
Thiol-ene candidate go / no-go	Yes, on time; extended	No go (poor mechanicals); changed to Go after 12 mos with VETHPB
Prepolymer evaluation	Yes, on time; extended	Original candidate failed to meet requirements, but successful alternative developed
Binder evaluation, go / no-go & down-select	Yes, +9 mos	Go, VETHPB selected
Propellant evaluation	Yes, +12 mos	VETHPB promising; ageing added
Draft report	Yes, +12 mos	Submitted
Final report	No	Need corrections from draft

Open Literature Bibliometrics

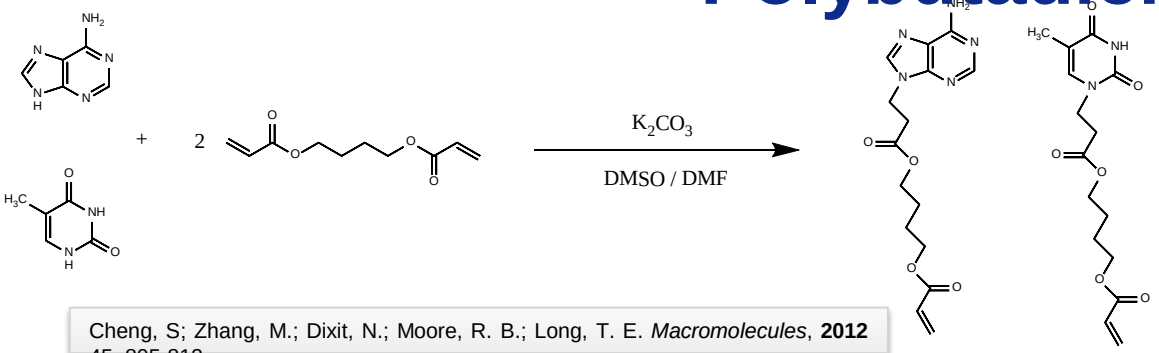
Type	# Complete	Comment
Journal articles	0	2 planned
Conference presentations	4	American Chemical Society meetings

Path Forward

- AFRL support for extended SEED will enable production of two 700 g (pint-scale mixes) in order to quantify mechanical properties at multiple temperatures of thiol-ene-based solid propellant, as well as gather hazard data. Designed experiments for propellant formulation are in progress. Better control of reaction rates through use of anti-oxidants that facilitate, rather than inhibit, cure, has been established.
- AFRL has a formally-funded effort for new binder development starting in FY17. Will utilize thiol-ene chemistry for some activities. Possible transition to propellant formulation after FY19.
- Development of thiol-ene chemistry through a full SERDP program would enable 1) joint service & university participation, 2) focus on environmentally-friendly oxidizers, and 3) accelerated work on propellant formulation rather than just binders.

Back Up Slides

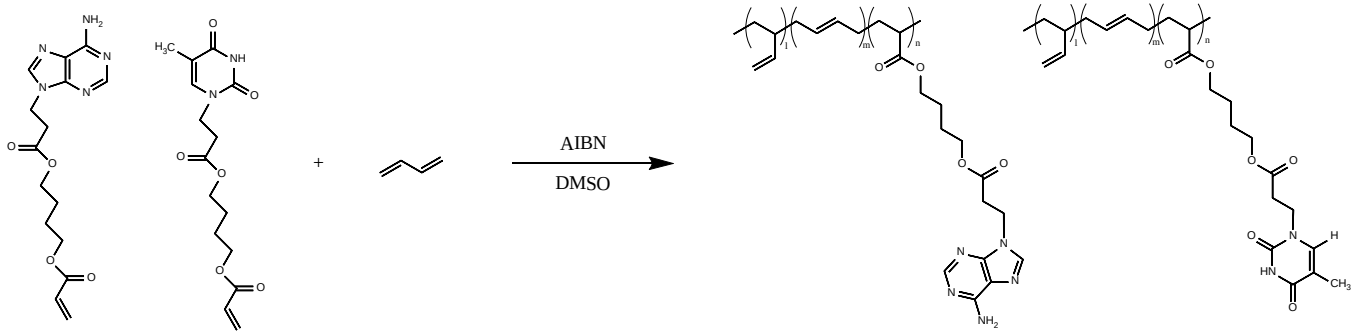
Incorporation of Nucleotide Bases in Polybutadiene

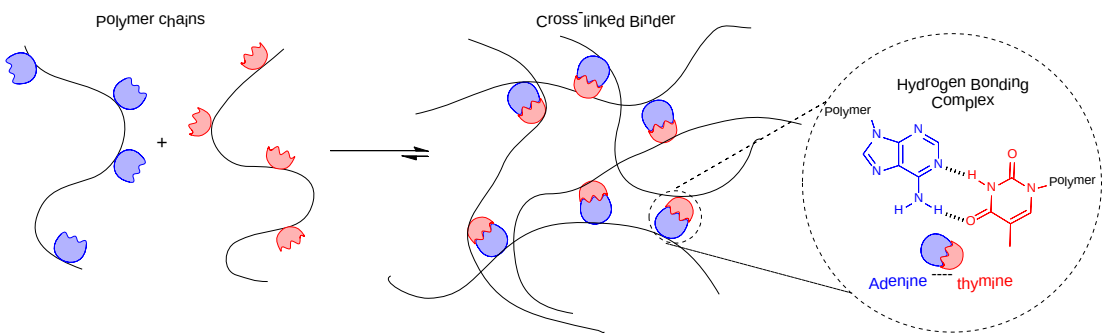


Adenine and thymine monomeric units were synthesized by Michael addition of a nucleobase with butanediol diacrylate. Incorporation of aliphatic spacer is expected to promote compatibility with HTPB and retention of desireable properties

Cheng, S; Zhang, M.; Dixit, N.; Moore, R. B.; Long, T. E. *Macromolecules*, **2012** 45, 805-812.

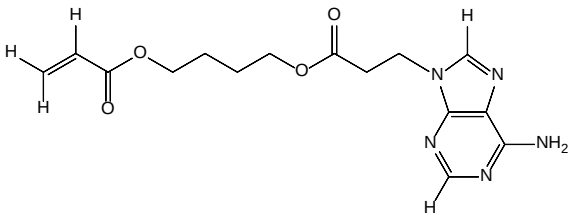
Copolymerization of either adenine or thymine methacrylate with butadiene gives an "A" and "B" complimentary copolymers

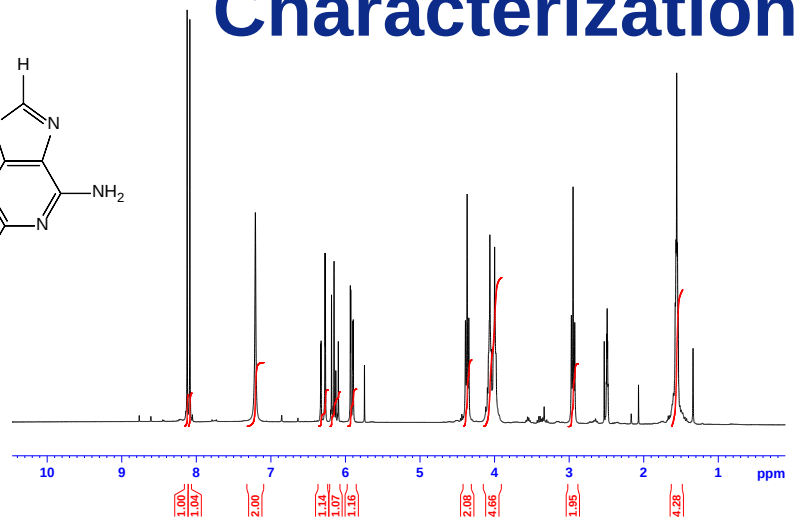




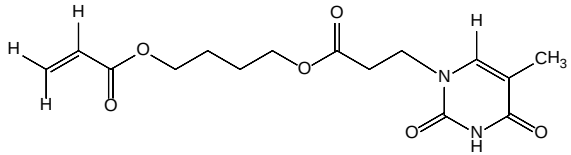
When in the presence of each other complimentary copolymers associate and form a crosslinked system consisting of hydrogen bonds

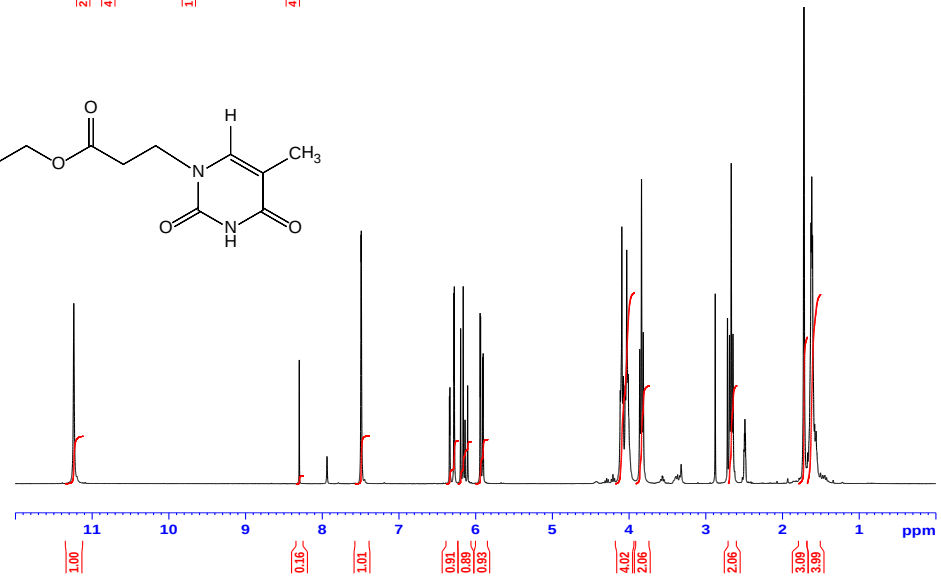
Adenine, Thymine Acrylate Characterization





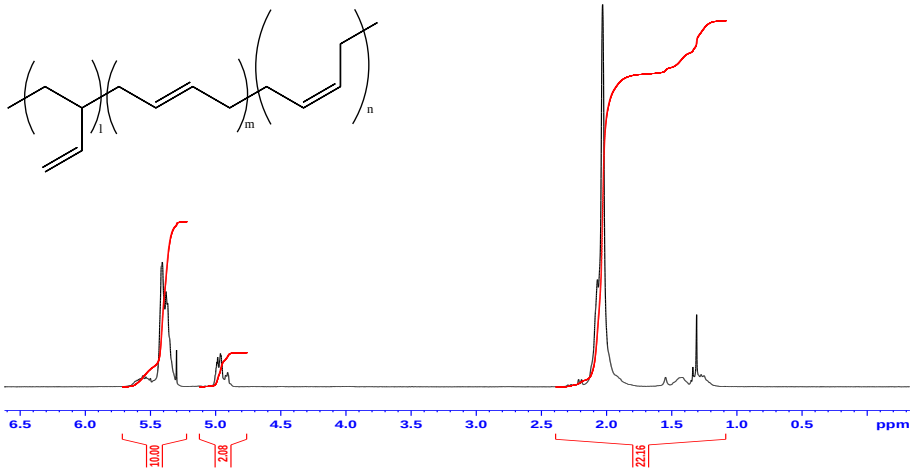
- N-9 substituted adenine acrylate was the major product. N-7 adduct and excess butanediol diacrylate was removed by flash chromatography
- NMR confirms N-7 addition
- Characteristic vinyl protons present with the expected integration



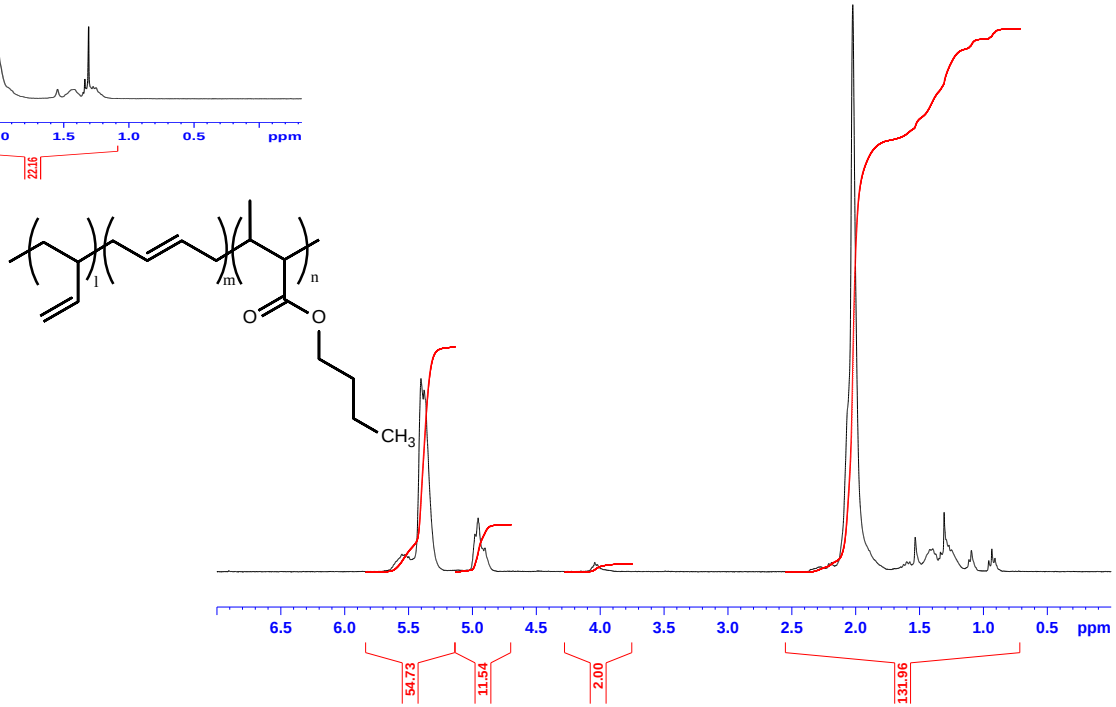


- N-1 substituted thymine acrylate was the major product.
- NMR confirms N-1 addition
- Characteristic vinyl protons present with the expected integration

Butadiene Polymerization / Butyl Methacrylate Copolymerization



- Optimization of butadiene polymerization performed in toluene with AIBN as initiator
- Polymerization performed at 70 °C for 48 hours at approximately 2 atm
- Polybutadiene contained 20% 1,2 addition
- Overall yield of ~20% was obtained from multiple polymerizations



- Due to the low yield of butadiene polymerization, copolymerization of butadiene with butyl methacrylate was performed to estimate expected incorporation of nucleobase acrylate with a given feed ratio
- Copolymerization of butadiene with butyl methacrylate was performed in toluene with AIBN as initiator
- Butyl acrylate incorporation of 3.2 mol% was obtained from a 2 mol% feed ratio
- Overall yield of 22% was consistent with butadiene homopolymerizations

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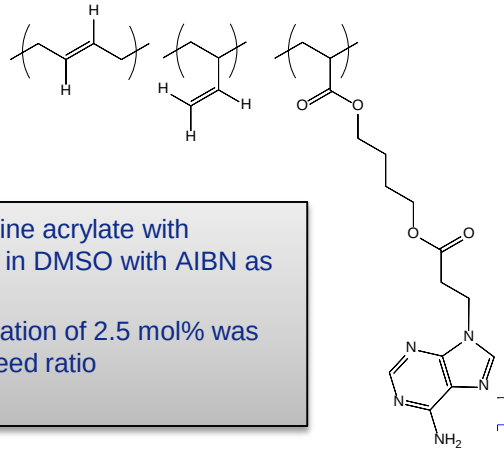
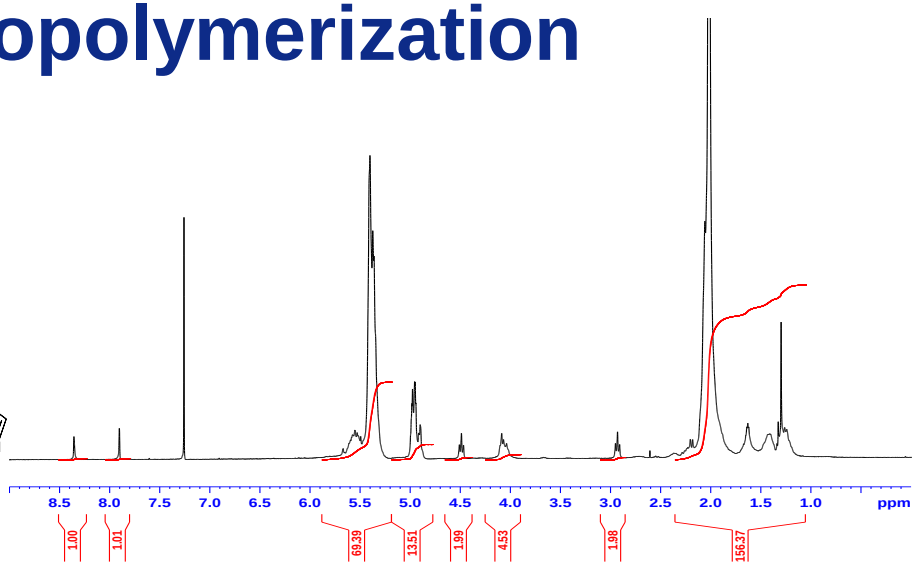
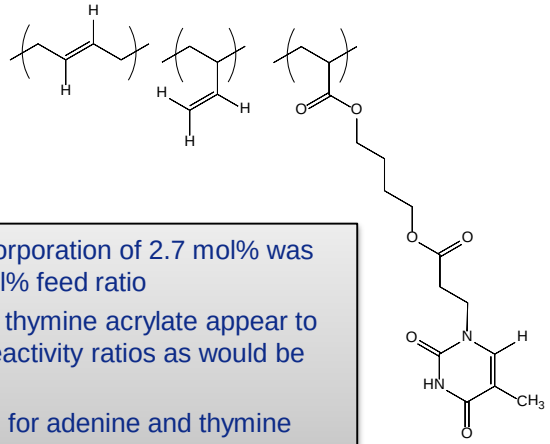
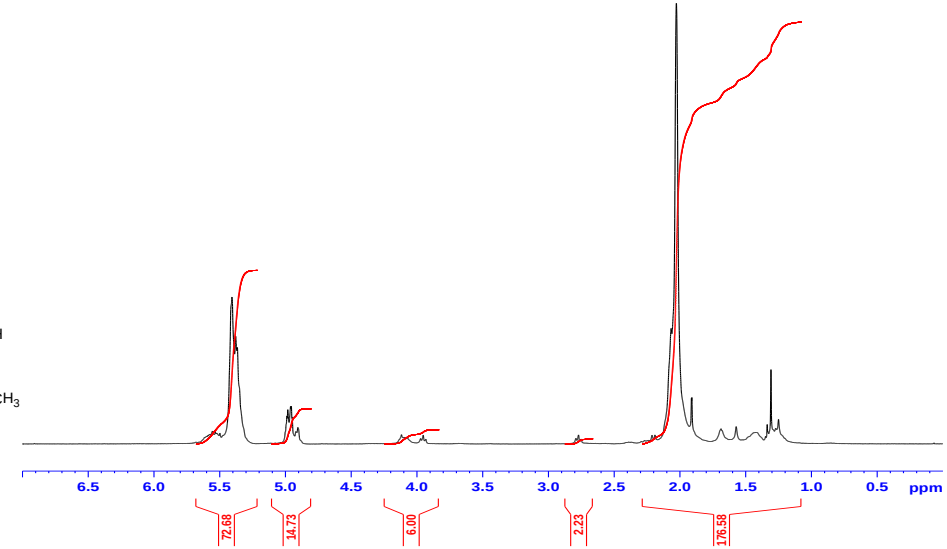
Adenine and Thymine Acrylate / Butadiene Copolymerization





- Copolymerization of adenine acrylate with butadiene was performed in DMSO with AIBN as the initiator
- Adenine acrylate incorporation of 2.5 mol% was obtained from a 4 mol% feed ratio





- Thymine acrylate incorporation of 2.7 mol% was obtained from a 4 mol% feed ratio
- Adenine acrylate and thymine acrylate appear to have near identical reactivity ratios as would be expected
- Overall yield of ~20% for adenine and thymine copolymerizations was consistent with butyl methacrylate copolymerization with butadiene

Long-Range Transition Plan

A full SERDP program in FY18-21 would complement AFRL binder development (FY17-19) and propellant development (FY20-22) efforts. A demonstration solid rocket motor would be produced in the mid 2020s through in-house efforts at AFRL, followed by prime-contractor led motor demonstration programs. Broader applications to areas such as warhead energetics would be pursued beginning with the full SERDP program.