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THE AIR FORCE RESEARCH LABORATORY
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Emergent cure chemistry in the development of aerospace materials

Andrew J. Guenthner, Josiah T. Reams, Jacob C. Marcischak, Michael D. Ford, Timothy S. Haddad, Joseph M. Mabry

ACS National Meeting
25 March 2015

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Outline

- **Goal**
  - Investigate polymeric cure systems with crosslinking chemistries that are unlikely to pose health concerns now and in the future
- **Objective**
  - Synthesis of new isocyante-free candidate binder formulations
  - Determine impact physical and mechanical properties
  - Demonstrate the use of new polymeric binders in binder formulation
- **Technical Challenges**
  - Maintain energy content and I_{sp}
  - New system must conform to current binder processing operations
  - Retention of physical and mechanical properties of HTPB / isocyanate systems
    - Low T_g
    - High elongation to break
    - Compatibility with high solids loading
- **Approach**
  - Nucleobase binding
  - Thiolene “click” chemistry

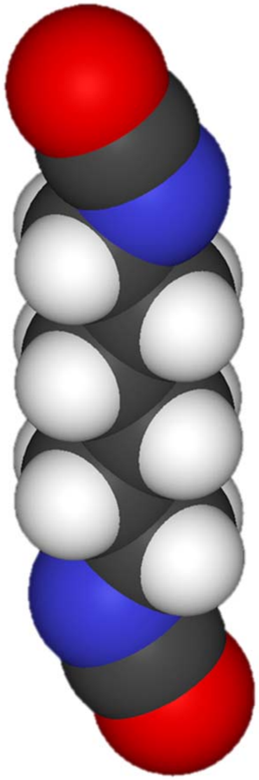
Acknowledgements:

- **Strategic Environmental Research and Development Program (SERDP)**
- **Air Force Office of Scientific Research, Air Force Research Laboratory – Program Support; PWG team members (AFRL/RQRP)**

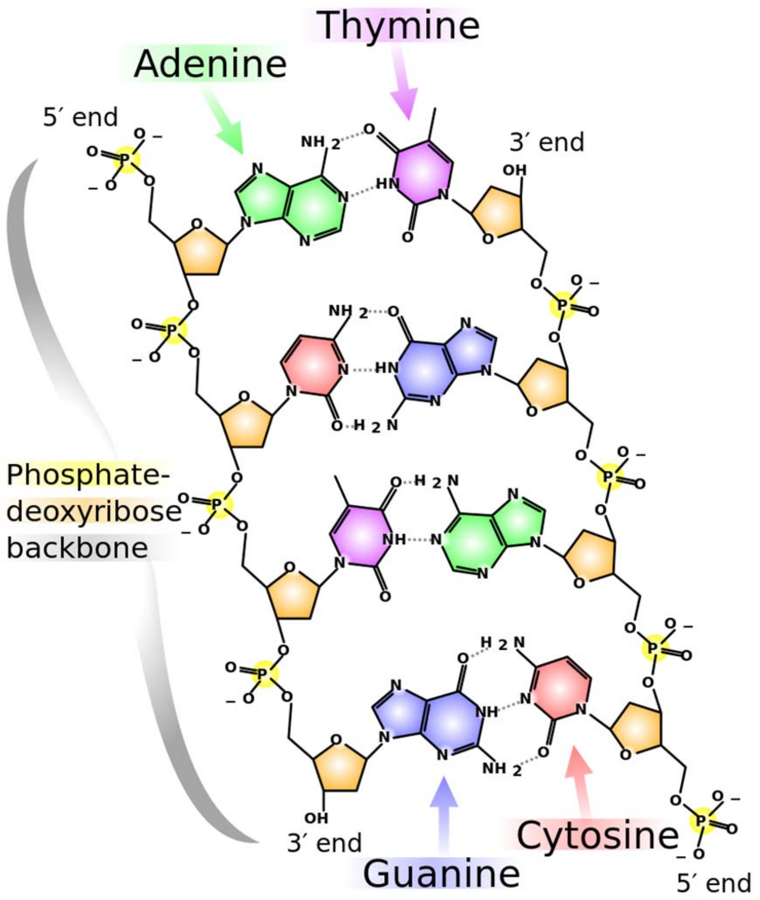
SERDP
DOD • EPA • DOE

Background: Isocyanates

- 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
- Increased regulation will result in increased cost and eventual unavailability in the U.S.

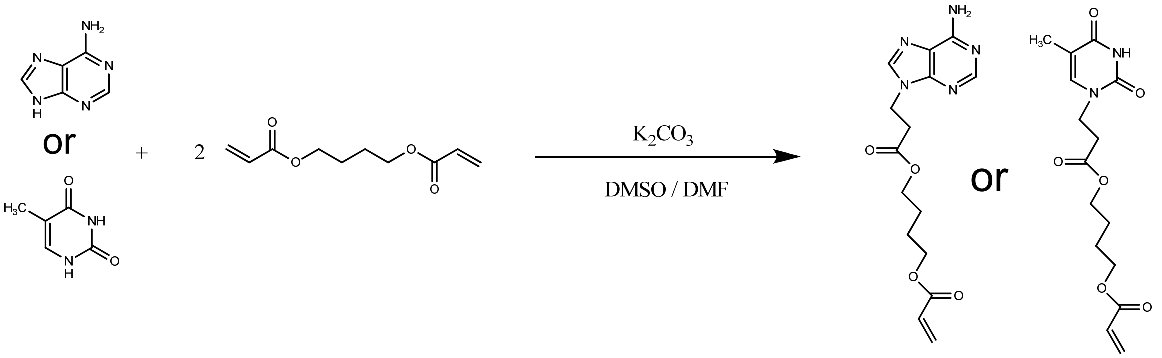


Nucleobase Binding



- **DNA is biologically ubiquitous therefore no current environmental regulation and likely no regulation in the future**
- **Potential advantages**
  - Dynamic covalent chemistry is a hot topic
  - Potential for self-healing properties
  - Reversible crosslinks have the potential for easy demilitarization
  - Insensitivity
- **Potential risks of nucleobase crosslinked polymer systems**
  - Polymers containing nucleobase monomers are rare and therefore are not commercially available
  - Properties not well understood

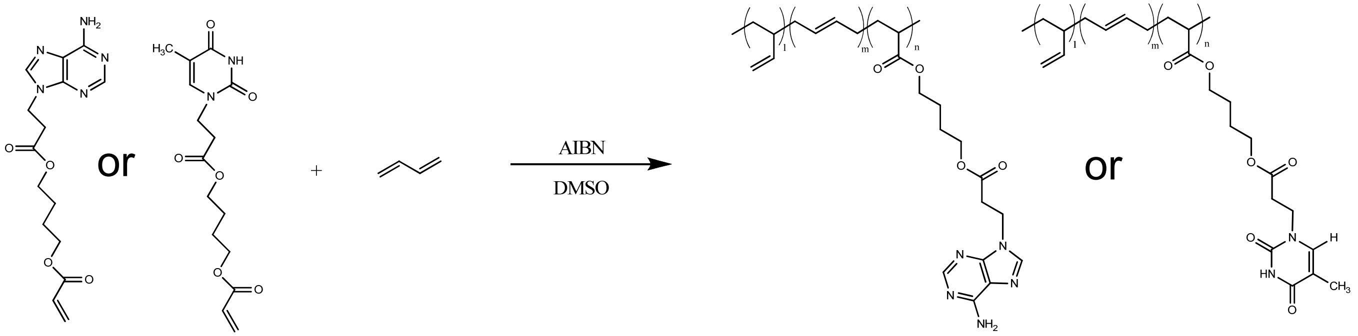
Incorporation of Nucleotide Bases in Polybutadiene

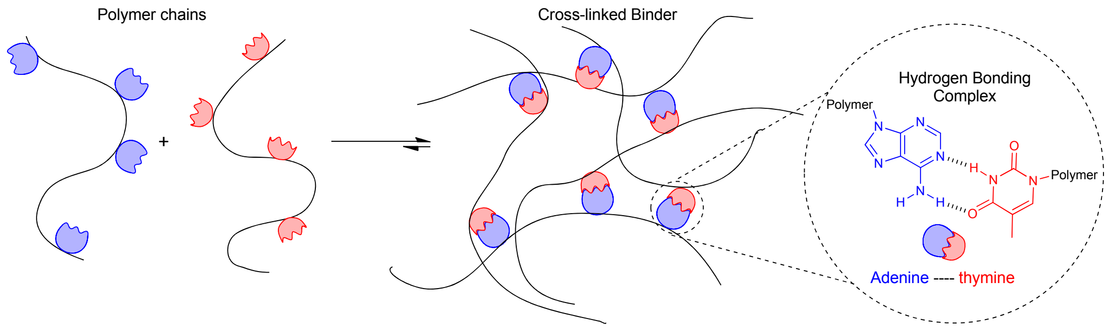


Adenine and thymine monomeric units were synthesized by Michael addition of a nucleobase with butanediol diacrylate. Incorporation of aliphatic spacer is expected to promote compatibility with HTPB and retention of desirable properties

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

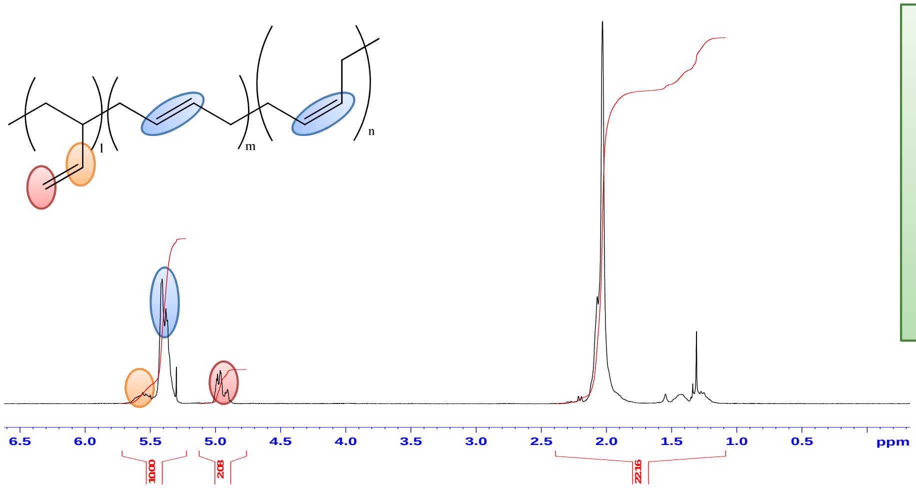
- Copolymerization of either adenine or thymine methacrylate with butadiene gives an “A” and “B” complimentary copolymers
- Nucleobases do not have the energy density of hydrocarbon therefore small amounts of nucleobase incorporation into polymers is desirable



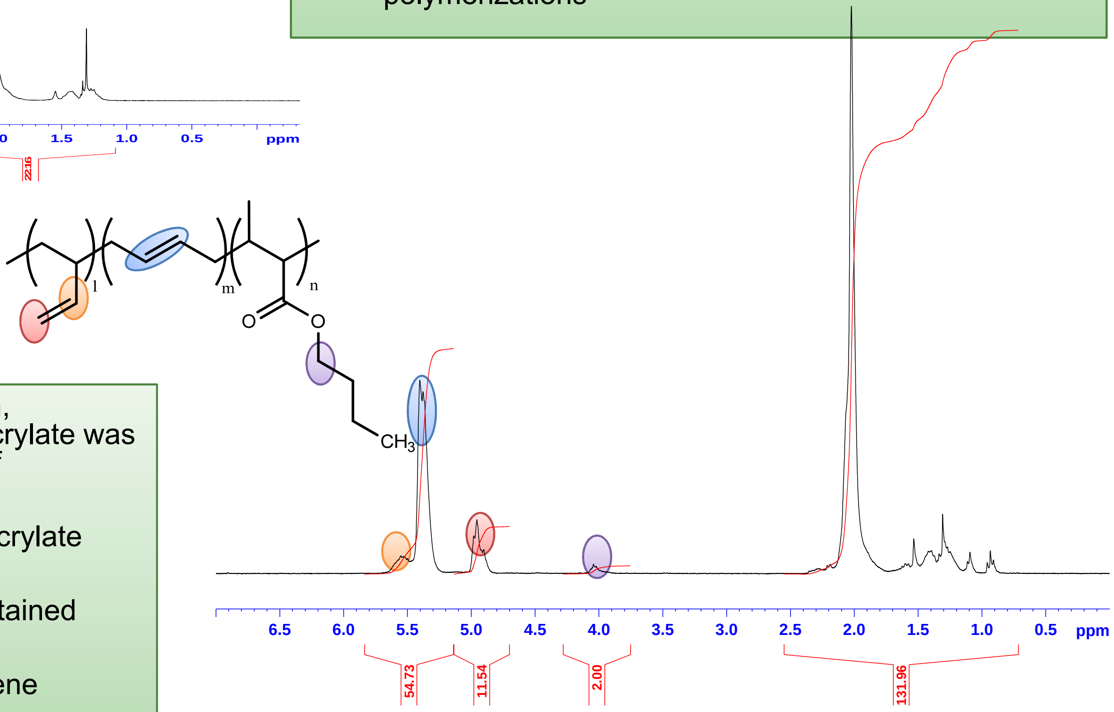


- When in the presence of each other complimentary copolymers associate and form a crosslinked system consisting of hydrogen bonds
- Both components exist as low viscosity liquids and do not self-associate
- When mixed together, the two part system is initially a low viscosity liquid that forms a crosslinked network as complimentary nucleobases associate

Butadiene Polymerization / Butyl Methacrylate Copolymerization



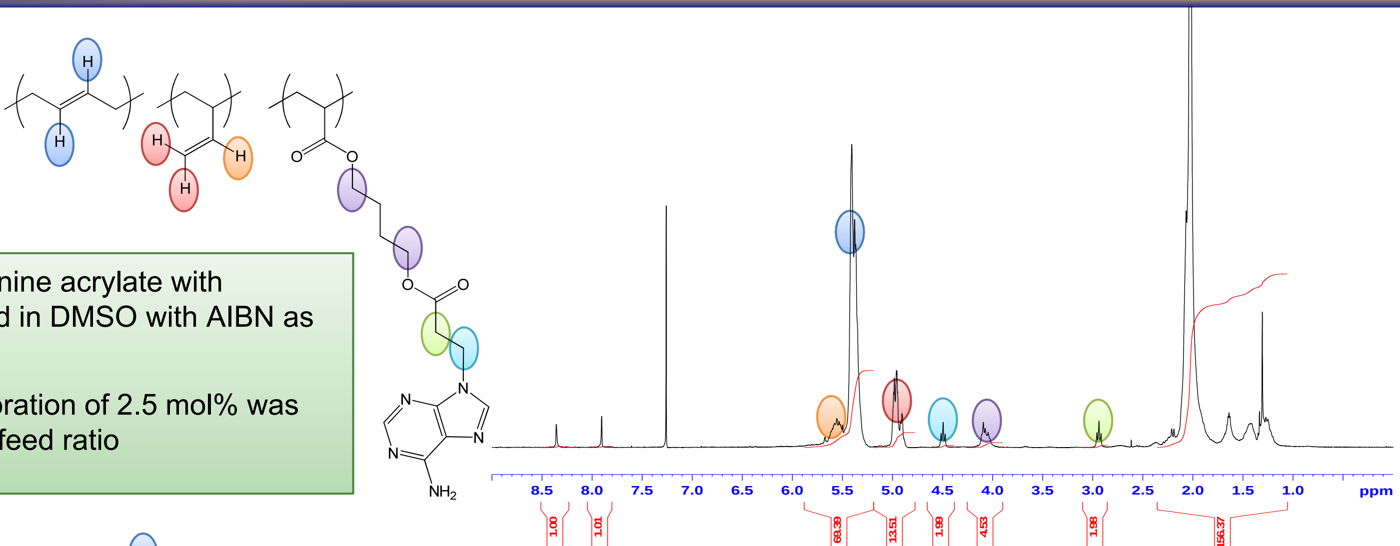
- Optimization of butadiene polymerization performed in toluene and DMSO with AIBN as initiator
- Polymerization performed at 70 °C for 48 hours at approximately 2 atm
- Polybutadiene contained 20% 1,2 addition
- Overall yield of ~20% was obtained from multiple polymerizations



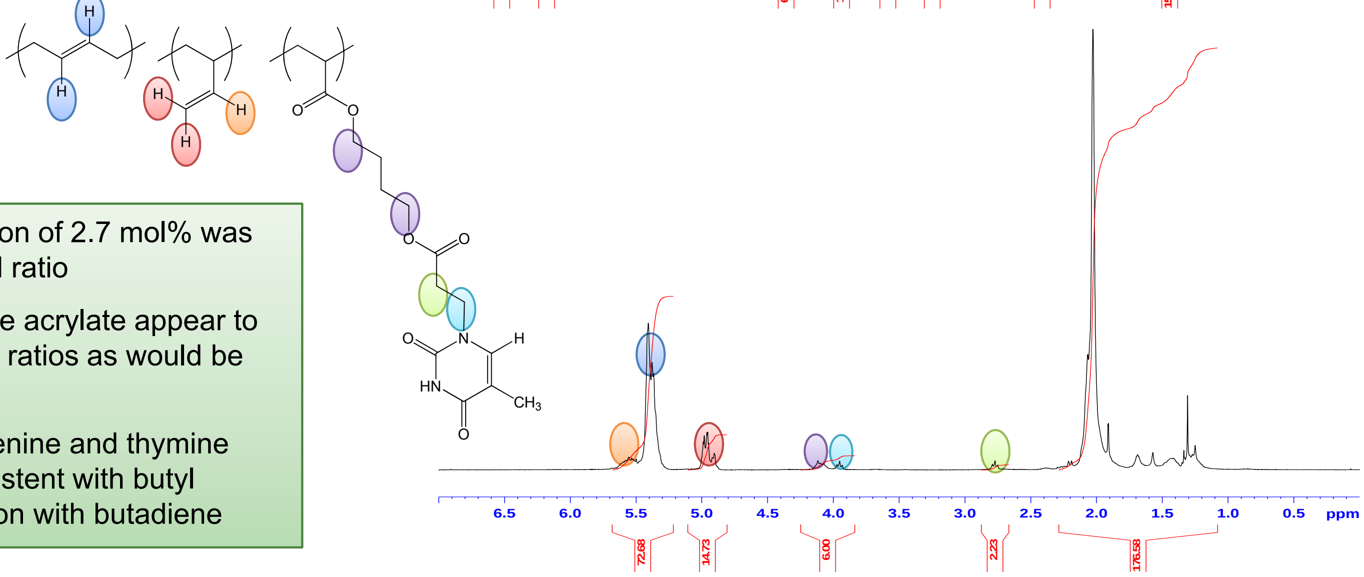
- Due to the low yield of butadiene polymerization, copolymerization of butadiene with butyl methacrylate was performed to estimate expected incorporation of nucleobase acrylate with a given feed ratio
- Copolymerization of butadiene with butyl methacrylate was performed in toluene with AIBN as initiator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

Adenine and Thymine Acrylate / Butadiene Copolymerization

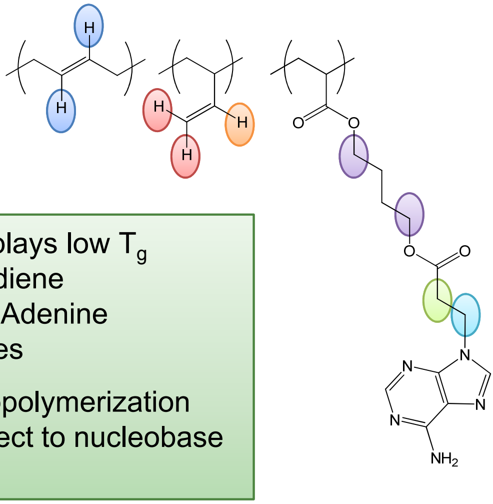
- Copolymerization of adenine acrylate with butadiene was performed in DMSO with AIBN as the initiator
- Adenine acrylate incorporation of 2.5 mol% was obtained from a 4 mol% feed ratio



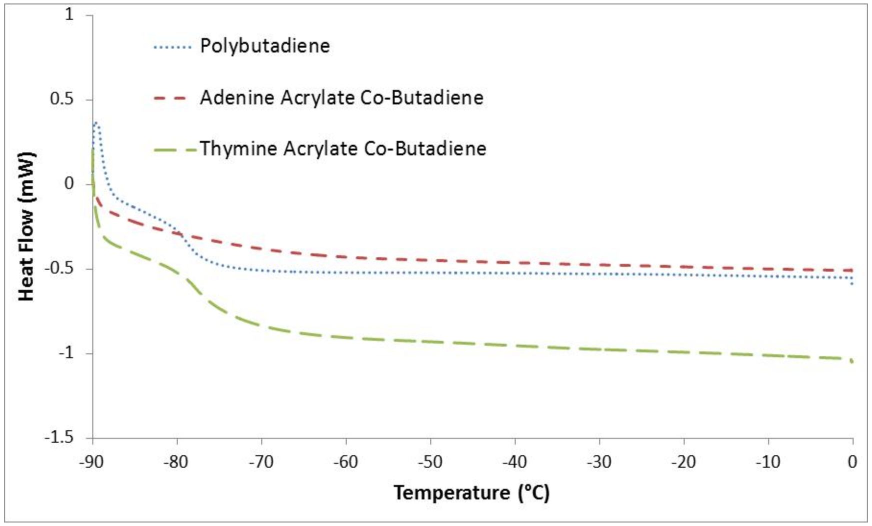
- Thymine acrylate incorporation of 2.7 mol% was obtained from a 4 mol% feed ratio
- Adenine acrylate and thymine acrylate appear to have near identical reactivity ratios as would be expected
- Overall yield of ~20% for adenine and thymine copolymerizations was consistent with butyl methacrylate copolymerization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



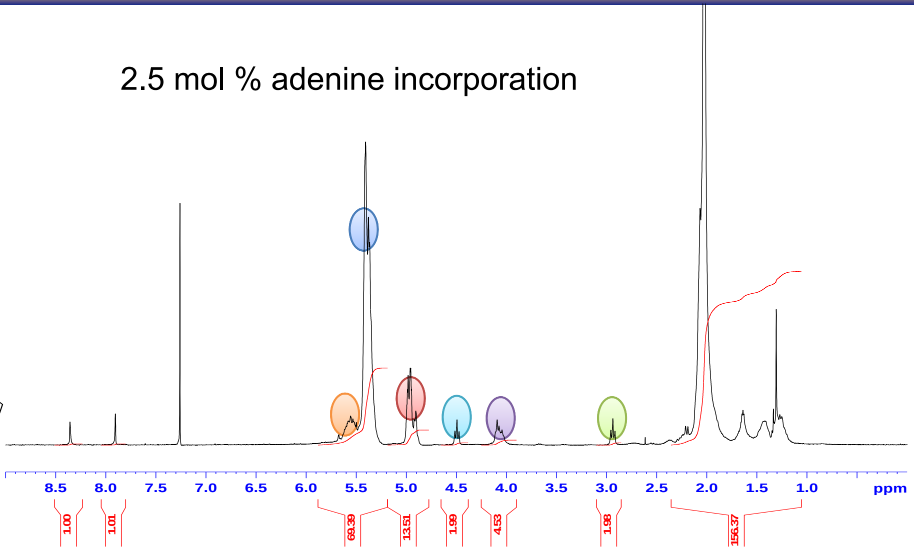
Adenine Acrylate Co-Butadiene Polymerization Variability



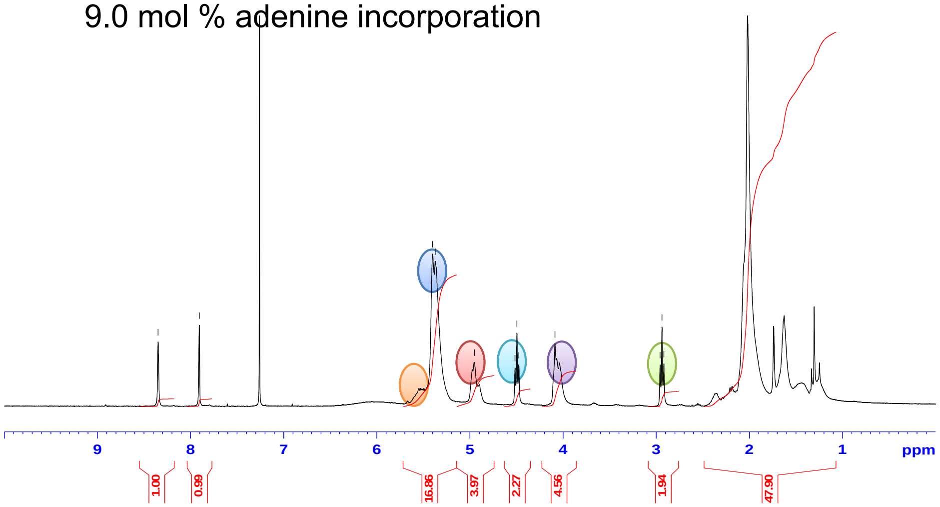
- Thymine copolymer displays low T_g comparable to polybutadiene homopolymer, however Adenine copolymer self associates
- Variability in Adenine copolymerization was observed with respect to nucleobase incorporation



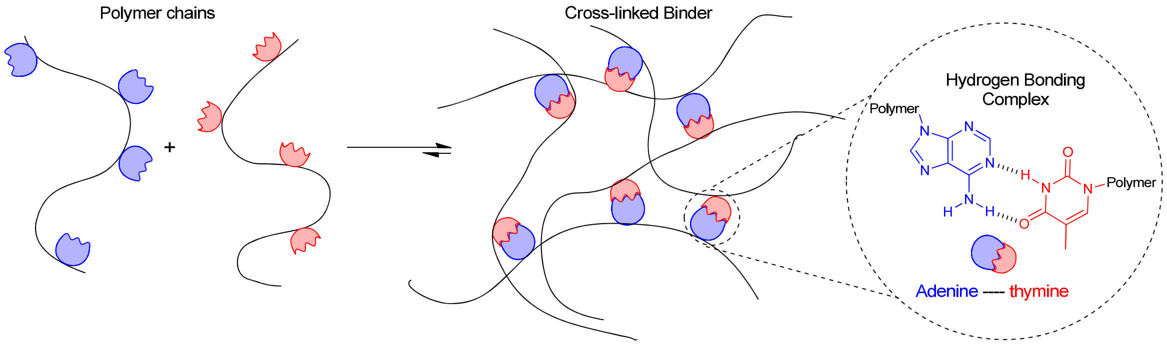
2.5 mol % adenine incorporation

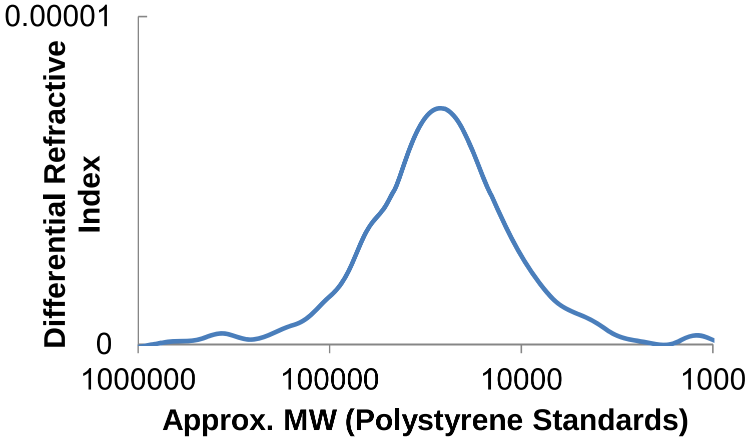


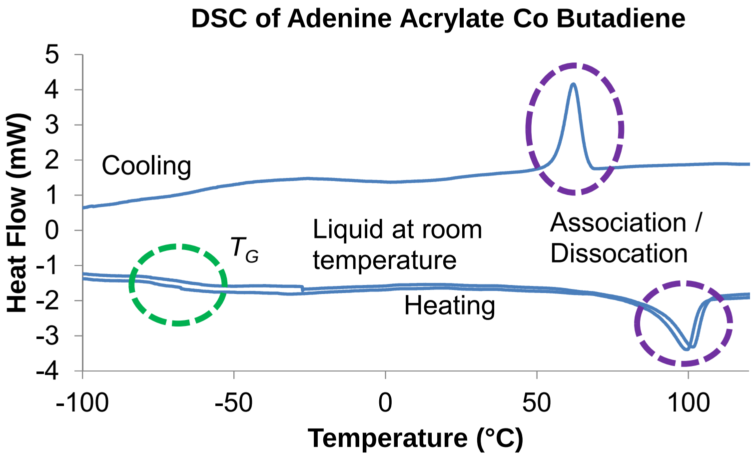
9.0 mol % adenine incorporation



DNA Nucleobase Polymer Properties

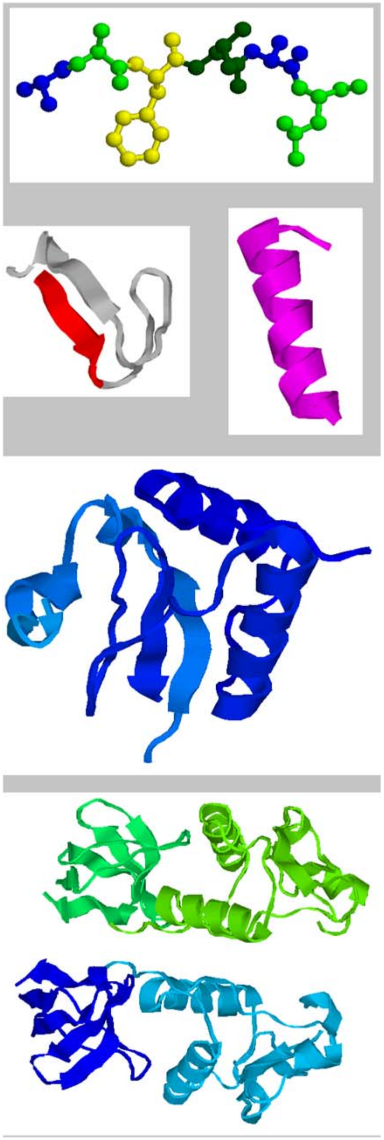


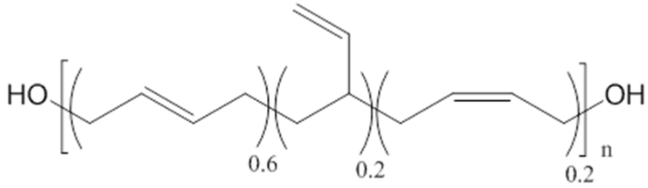




- **In polar media adenine units do not self associate, however non-polar media promotes self-association**
- **Self association of individual “part A” or “part B’ components makes mixing of two components difficult**
- **Too many unknown characteristics of self- and cross-association for near-term development of reliable cross-linking substitute**

Carbon-Sulfur Bonds as Crosslinks

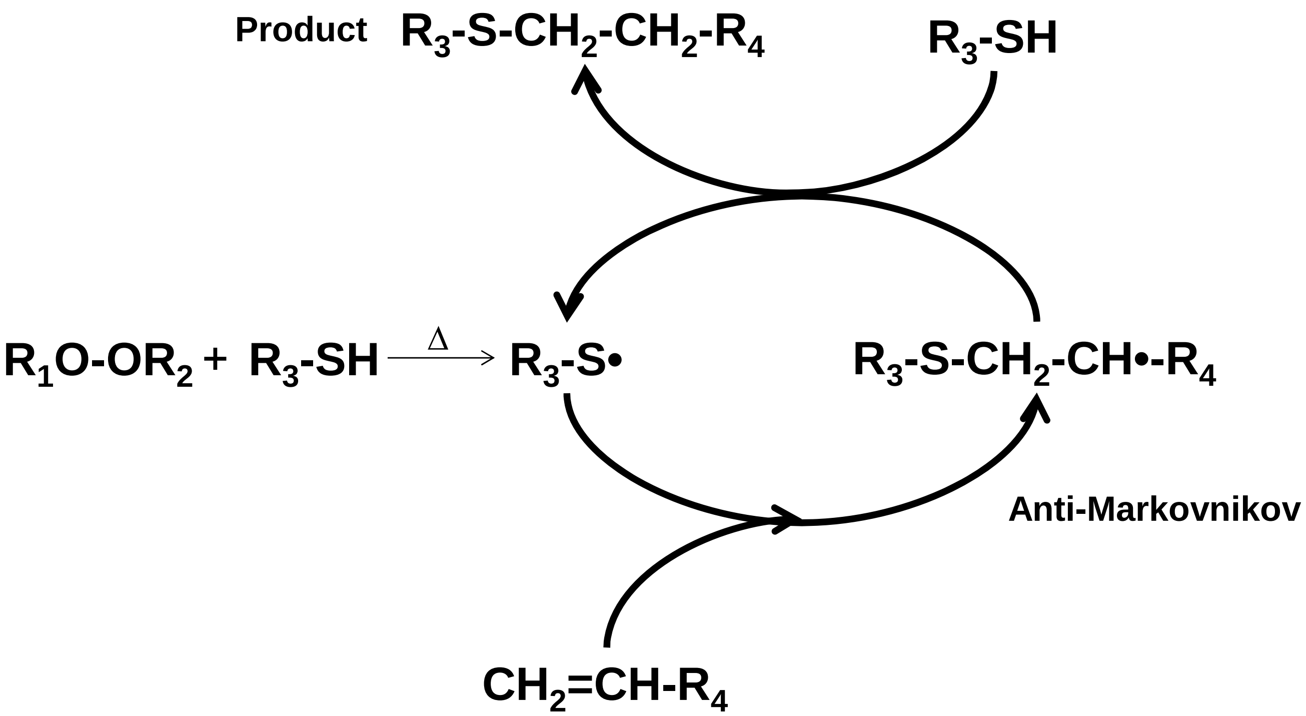




$HSCH_2(CH_2)_7CH_2SH$

- **Many sulfur containing compounds exist in nature including proteins**
- **Thiol-ene chemistry not biologically ubiquitous like nucleobase binding**
- **Thiol-ene chemistry similar to free radical in terms of reactivity but with more control and selectivity**
- **Utilization of existing vinyl double bonds in commercial polybutadiene**

Thiol-Ene Chemistry



Product $R_3\text{-S-}CH_2\text{-}CH_2\text{-}R_4$

$R_3\text{-SH}$

$R_1O\text{-}OR_2 + R_3\text{-SH} \xrightarrow{\Delta} R_3\text{-S}\bullet$

$R_3\text{-S-}CH_2\text{-}CH\bullet\text{-}R_4$

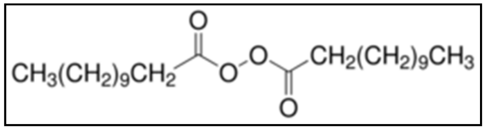
Anti-Markovnikov

$CH_2\text{=}CH\text{-}R_4$

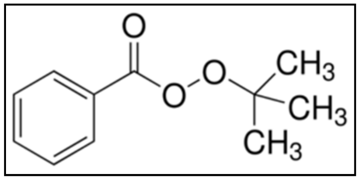
- **Thiol-ene chemistry is a hybrid of free radical and condensation chemistry. It combines the speed and ease of initiation of free radical chemistry with the product specificity of condensation chemistry.**
- **As a type of "click" chemistry, it generates no volatiles and minimal side products.**

Peroxide Catalyzed Thiol-ene Click

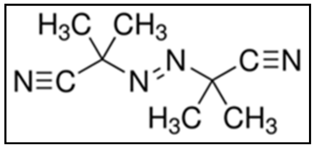
Peroxides



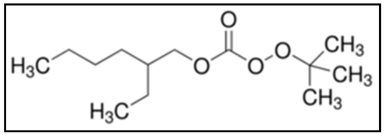
Lauroyl Peroxide
Luperox ® LP
64 °C



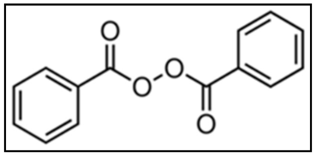
t-butyl peroxybenzoate
Luperox ® P
104 °C



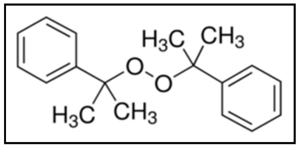
AIBN



t-butylperoxy 2-ethylhexyl carbonate,
Luperox ® TBEC
100 °C

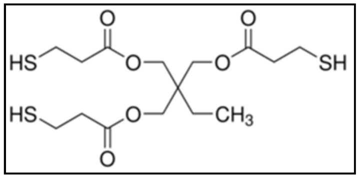


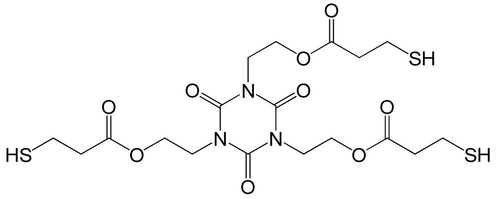
Benzoyl Peroxide
73 °C



Dicumyl Peroxide
117 °C (DCP)

Thiols



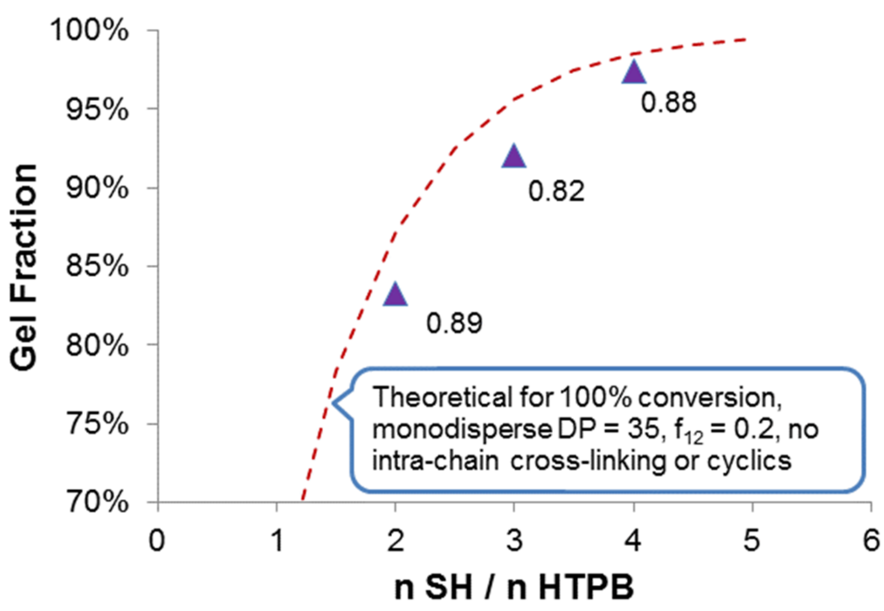


$HSCH_2(CH_2)_7CH_2SH$

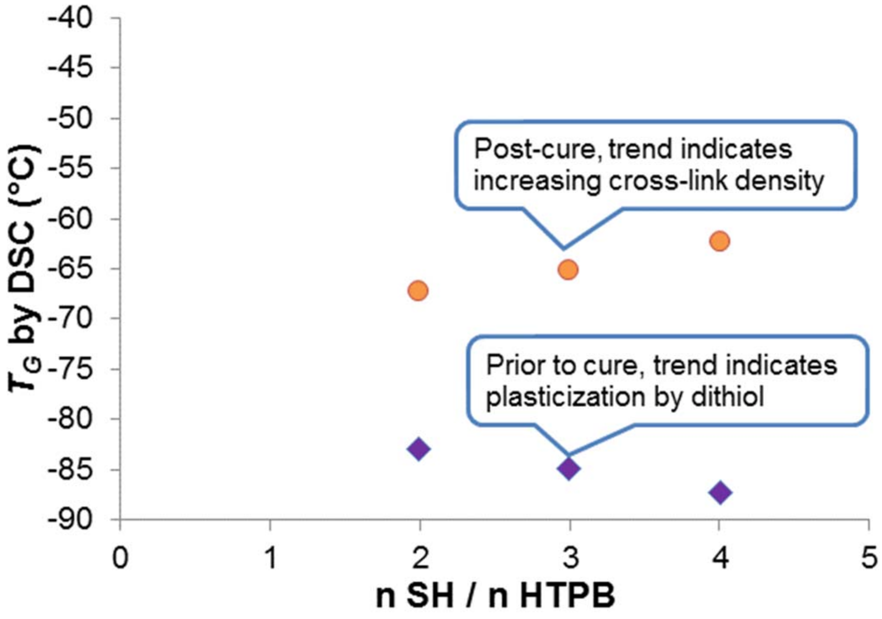
1,9-Nonanedithiol, 95%

- Many available peroxide initiators with different 10 hour half-life temperatures allow reactivity to be tuned to processing conditions
- Ratio of peroxide to thiol can be varied to tune rate of initiation
- Choice of thiol affects crosslink density and hydrolytic stability
- TBEC initiated nonanedithiol /HTPB cure was chosen to match current HTPB-isocyanate processing conditions at 60 °C

Thiol-ene Crosslinked HTPB



Theoretical for 100% conversion, monodisperse DP = 35, f_{12} = 0.2, no intra-chain cross-linking or cyclics

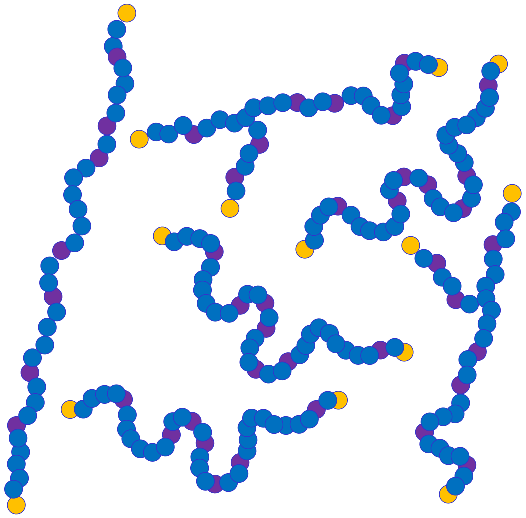


Post-cure, trend indicates increasing cross-link density

Prior to cure, trend indicates plasticization by dithiol

- **HTPB cured with 1,9-nonanedithiol / TBEC (peroxide) at 5:1 SH / O•, 60 °C, for 8 days under N_2. Data point labels (left figure) indicate fraction of available –SH incorporated into gel, a measure of conversion.**
- **Glass transition temperatures remain at acceptable levels over a wide range of cure conditions**

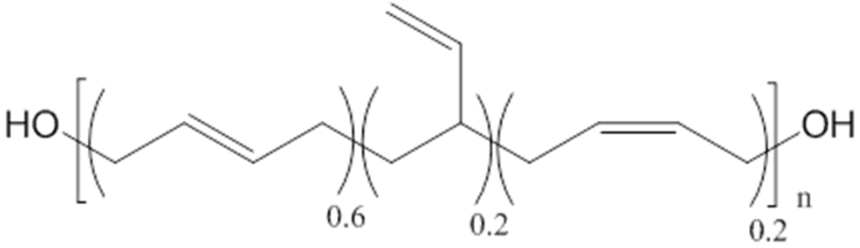
Importance of Network Architecture



Chain backbone (1,4 addition)

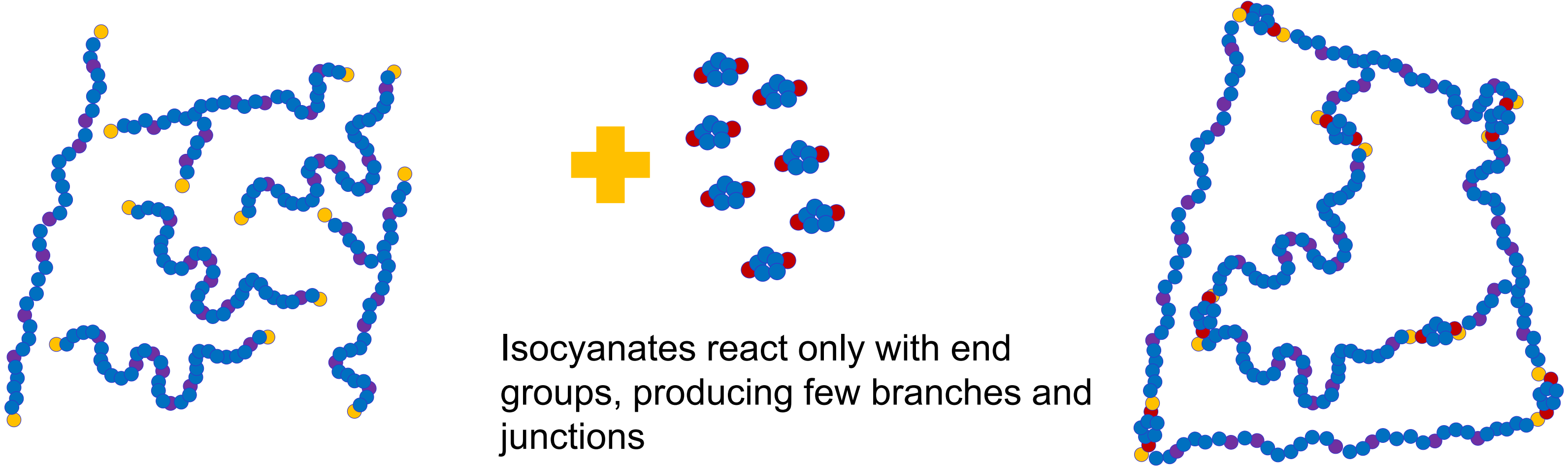
Vinyl goups (1,2 addition)

Hydroxyl end groups

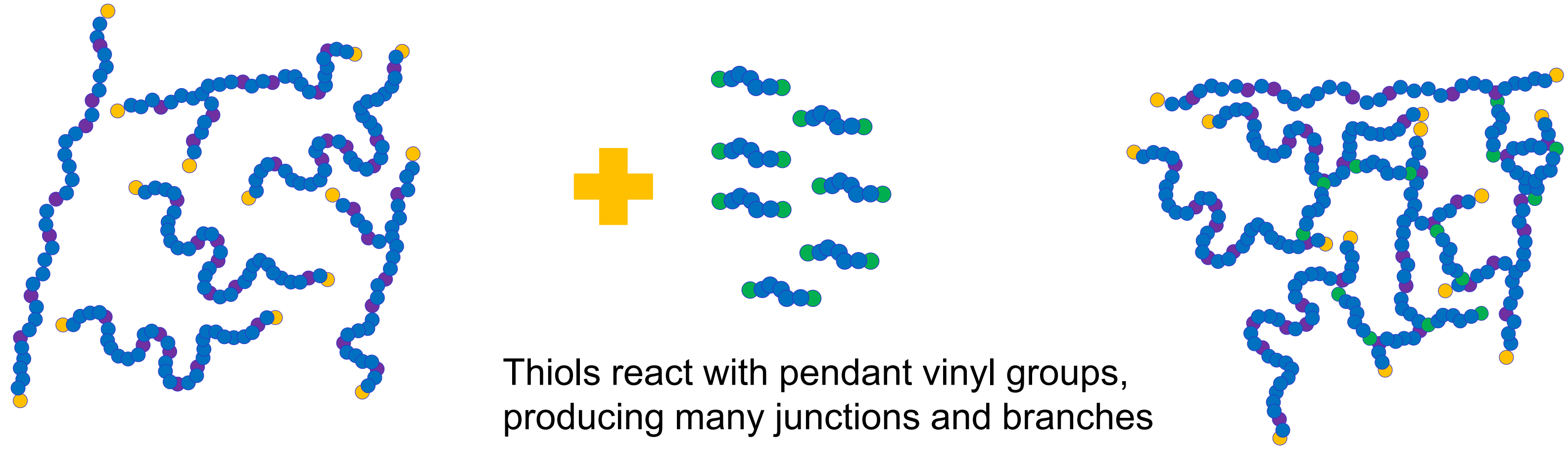


- Free radical polymerized HTPB
  - Mixture of 1,4 and 1,2 addition
  - Hydroxyl end-group functionality 2.4-2.6 / per chain
  - T_g -75 °C
  - Molecular Weight M_n = 2800 g/mol
  - Polydispersity ~2.5

Importance of Network Architecture



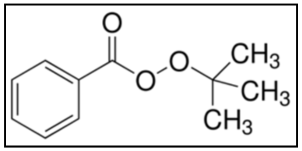
Isocyanates react only with end groups, producing few branches and junctions



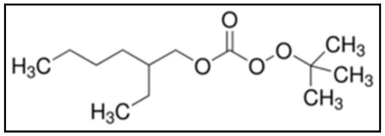
Thiols react with pendant vinyl groups, producing many junctions and branches

Reproduction of correct polymer architecture is necessary to obtain correct mechanical properties

Thiol-ene cured HTPB Modulus



Luperox® P



Luperox® TBEC

Peroxide	Thiol	SH:HTPB	Theoretical Modulus (psi)	Measured Modulus* (psi)
Luperox P	1,9 Dithiol	3:1	*215*	*141*
Luperox P	1,9 Dithiol	4:1	*360*	*331*
TBEC	1,9 Dithiol	3:1	*492*	*419*
TBEC	1,9 Dithiol	4:1	*851*	*502*

*Compressive modulus at 298K measured by thermomechanical analysis (TMA)

- Mechanical property data suggests thiol-ene cured HTPB has a lower molecular weight between crosslinks and isocyanate cured HTPB
- Reaction at chain ends rather than at pendant vinyl groups is necessary to achieve correct architecture and mechanical properties

Strategies for Correct Architecture

- **HTPB without vinyl side groups**
- **Polybutadiene (PB) with low vinyl incorporation**
  - Polybutadiene with 1% vinyl
    - Difficult to tell the position of vinyl groups on polymer chain
    - Initial investigation with nonanedithiol cure produces elastomeric material
- **Thiol-terminated polyethylene glycol (PEG) system**
  - Co-cured with di and tri-functional vinyl compounds
  - Demonstration of principle in progress
- **Thiol-terminated polybutadiene**
  - Co-cure with di and tri-functional vinyl groups
  - Presence of main chain vinyl groups will result in intramolecular reaction / cyclization
  - Synthesis of polybutadiene with di-anionic initiator to produce cis-1,4 substituted polybutadiene

Impact of Results on Future DoD Operations

- **Elimination of isocyanates alleviates a major occupational health and safety concern in the manufacture and use of solid rocket motor propellants**
- **Elimination of isocyanates also mitigates issues related to moisture sensitivity during propellant mixing and casting, and may reduce some forms of degradation during long-term storage in humid environments**
- **Replacement of isocyanates with chemical groups that are ubiquitous in the biosphere will greatly reduce the risk associated with future regulation / obsolescence throughout the manufacturing, use, and de-militarization life cycle**
- **Alternative cure chemistries that are successful for solid rocket motors may be transitioned to other applications, such as paints, foams, sealants, and adhesives that also represent a significant source of occupational health risk for DoD and DOE**

Future Effort and Transition Plans

- **Project focus shifting towards demonstration of energetic propellant formulations**
- **If energetic formulations demonstrate acceptable properties, then a full SERDP program utilizing thiol-ene cured binders will be proposed**

Conclusions

- Increasing regulation of isocyanates in the workplace poses a significant, but not insurmountable, challenge to DoD/DOE operations
- DNA nucleobase technology represents a promising future path to isocyanate replacement, but is not yet mature enough for near-term development in solid rocket motors
- Thiol-ene chemistry represents a safer alternative to isocyanate chemistry that remains a promising candidate for near-term development in solid rocket motor propellants
- When paired with the proper polymer architecture, thiol-ene based propellants will offer simpler manufacturing, improved quality control, greatly reduced occupational health and safety concerns, and some potential decrease in humid ageing in solid rocket motor propellants

QUESTIONS?

U.S. AIR FORCE