# Facile Chain-End Modification of RAFT Polymers

Shelby Shankel

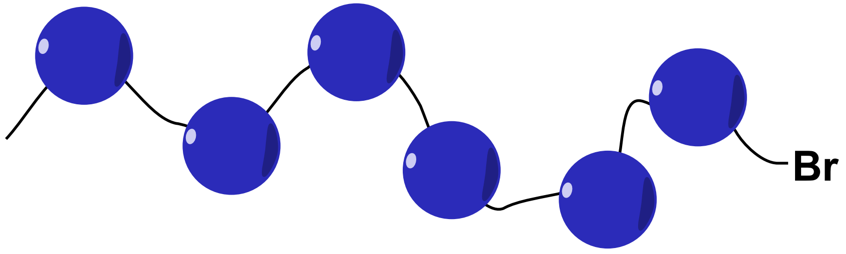
CCS Chemistry, UCSB

Emre Discekici

Read de Alaniz Group, Chemistry and Biochemistry

MARC U-STAR, NIH

# Importance of Modification



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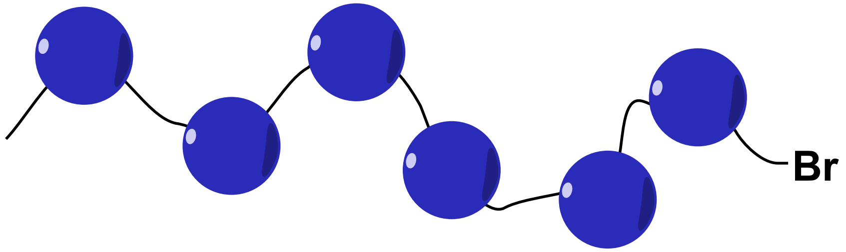


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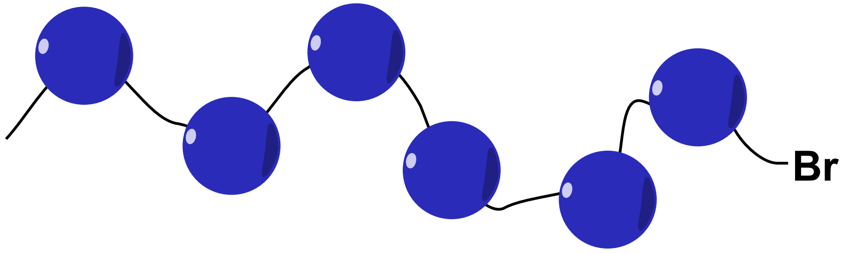


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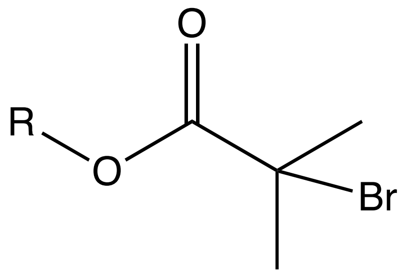
- Example: block copolymers

ATRP initiator



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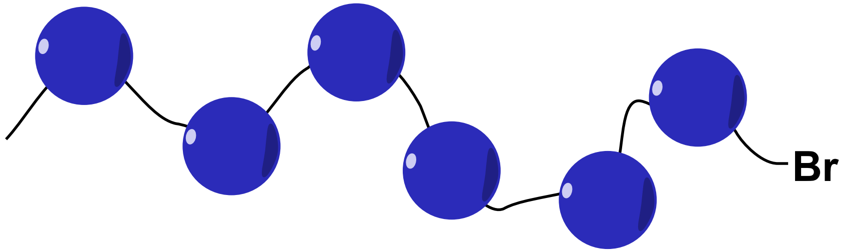


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- Example: block copolymers
  - Adhesives, rubber

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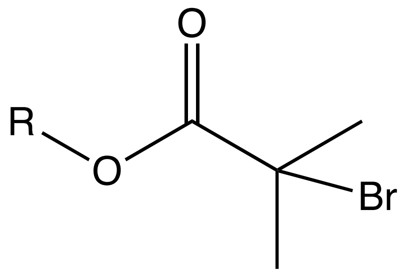


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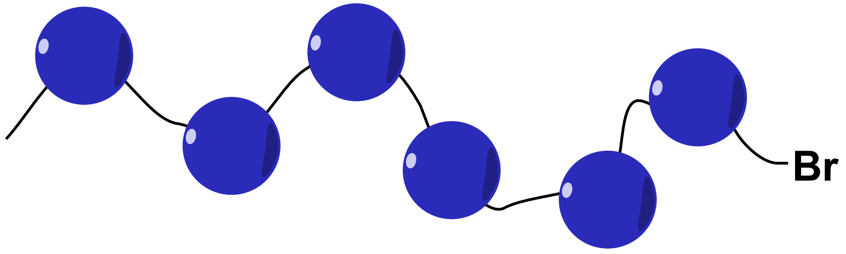


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- Example: block copolymers
  - Adhesives, rubber
  - Micelles

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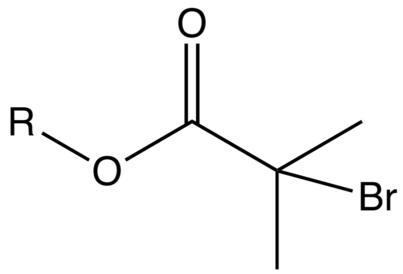


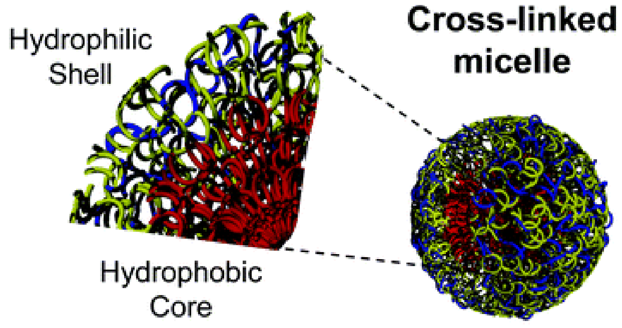

# Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerization

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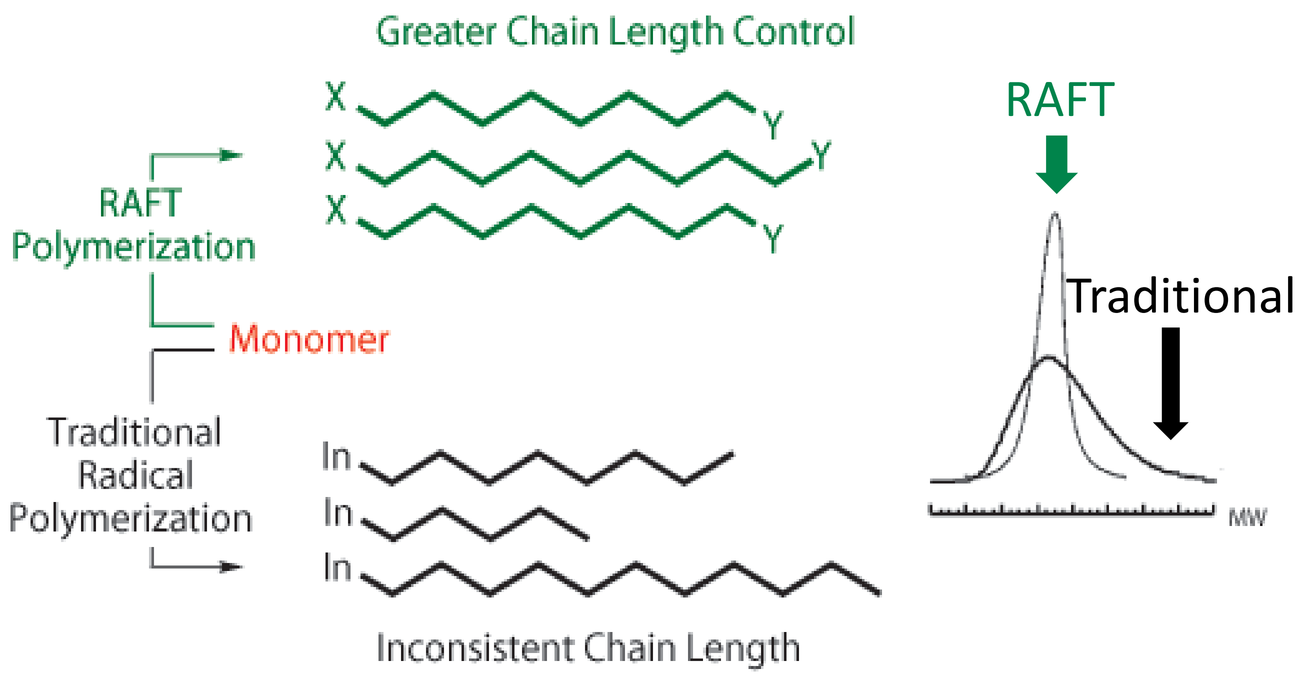
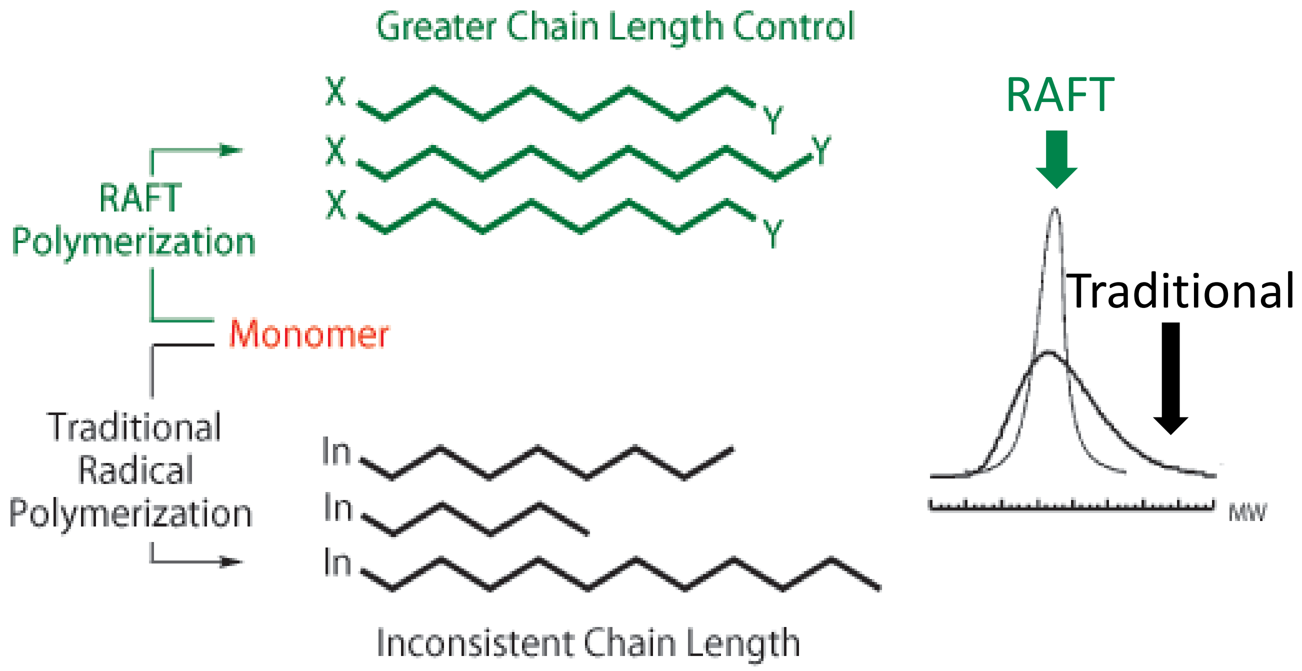


# Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerization

- Controlled radical polymerization
  - Control of molecular weights
  - Narrow polydispersity index



# Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerization

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NIH National Institutes of Health

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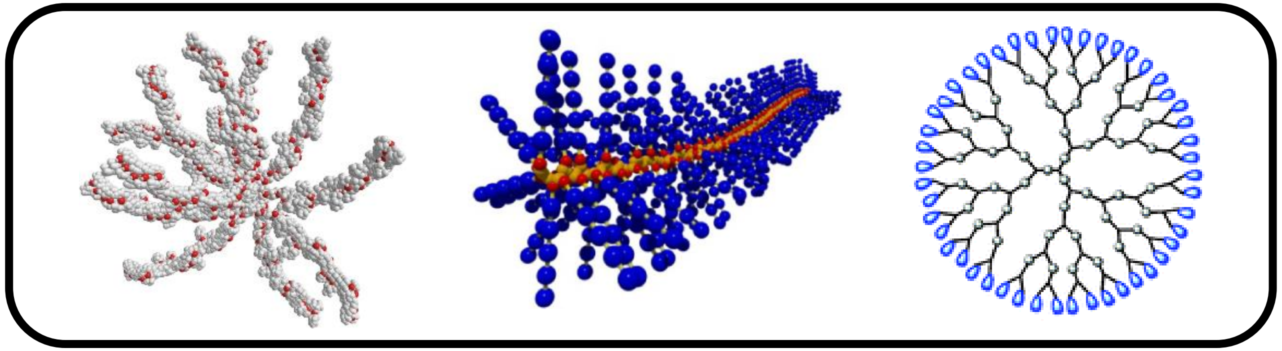

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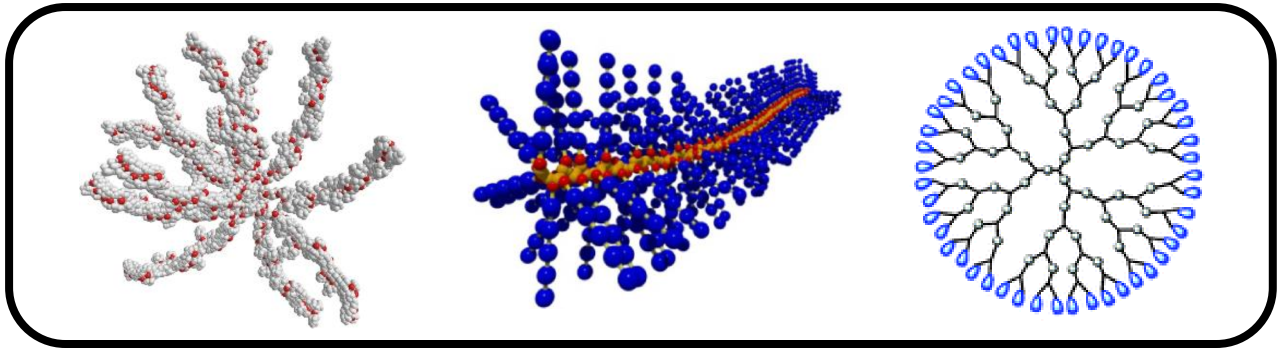

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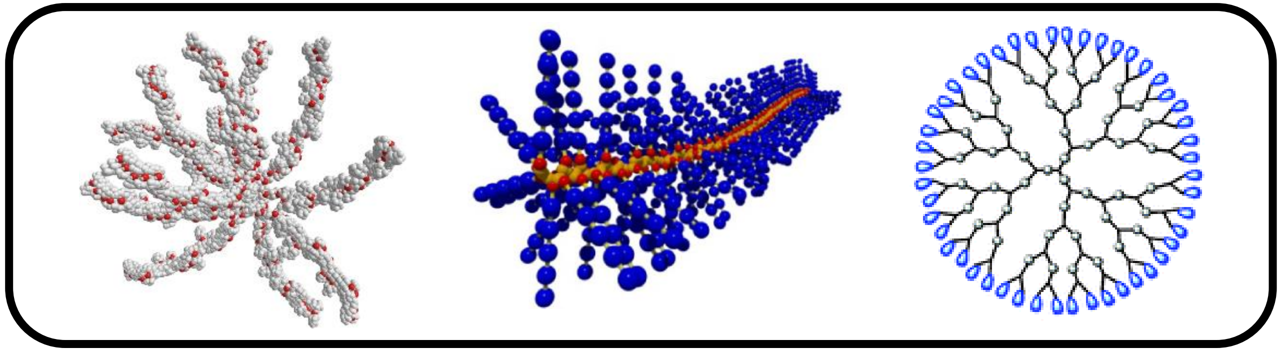

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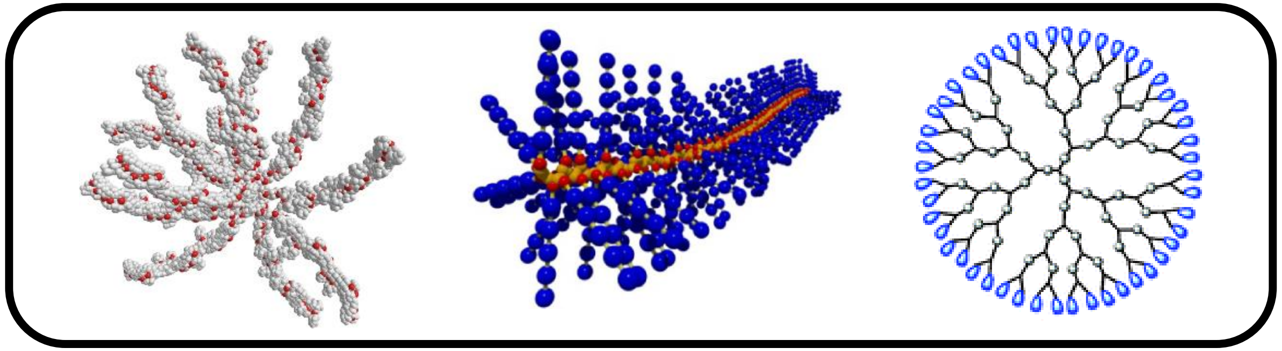
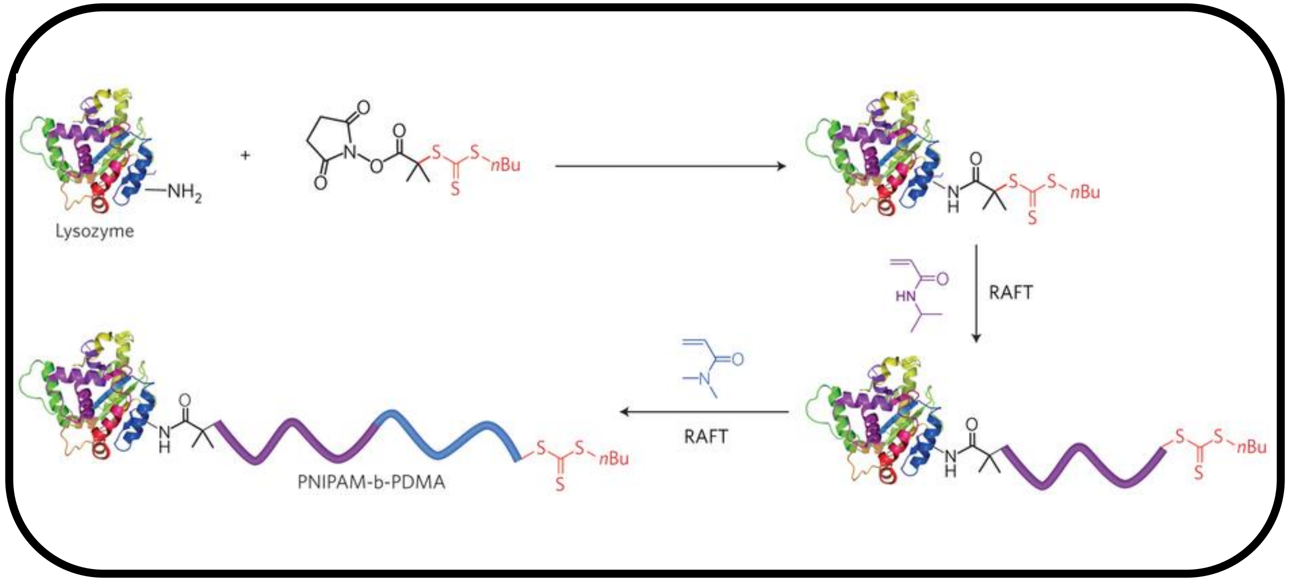
- Controlled radical polymerization
  - Control of molecular weights
  - Narrow polydispersity
- Why RAFT?
  - Tolerance of functional groups
  - Formation of complex structures
  - High conversions
  - Water soluble
  - Useful in biomedical applications





# Current Challenges with RAFT

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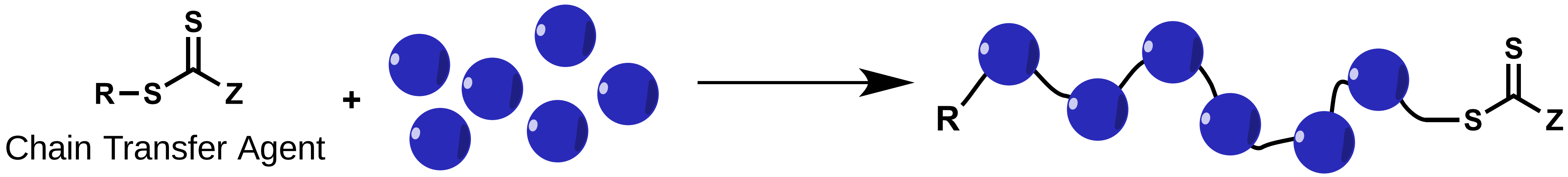

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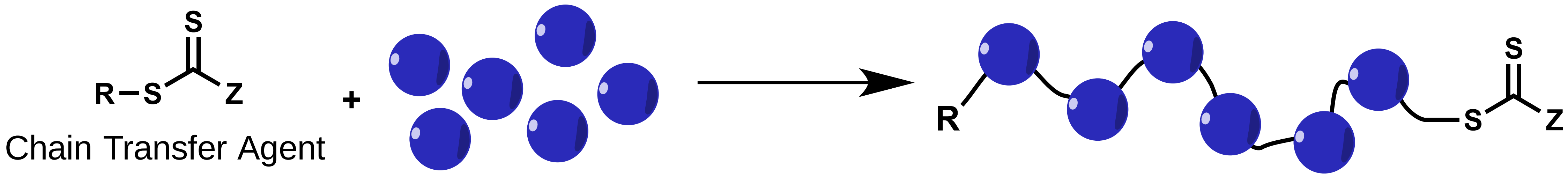
- Conjugation of chain end



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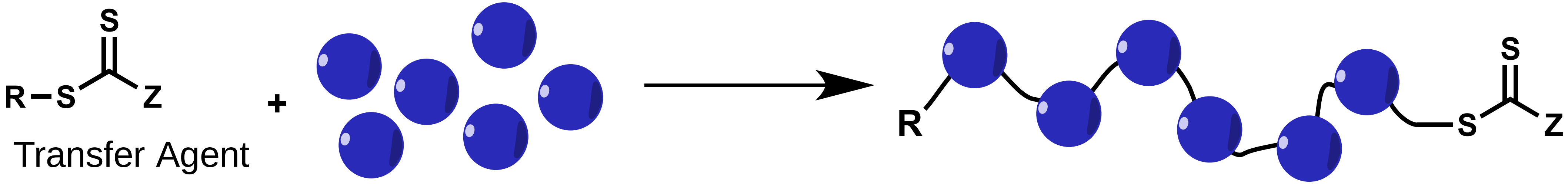
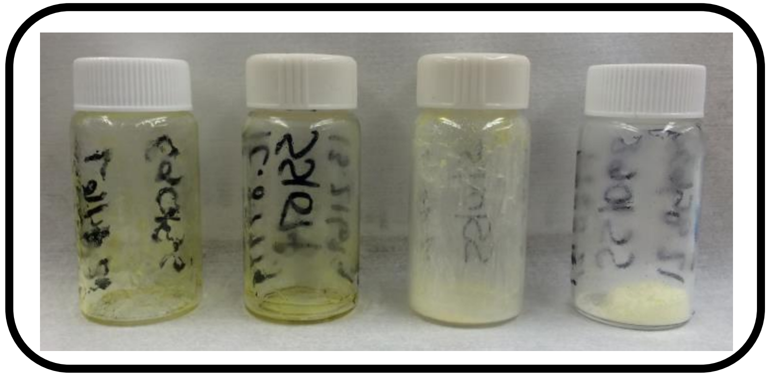
- Conjugation of chain end
  - Discoloration




Chain Transfer Agent



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- Conjugation of chain end
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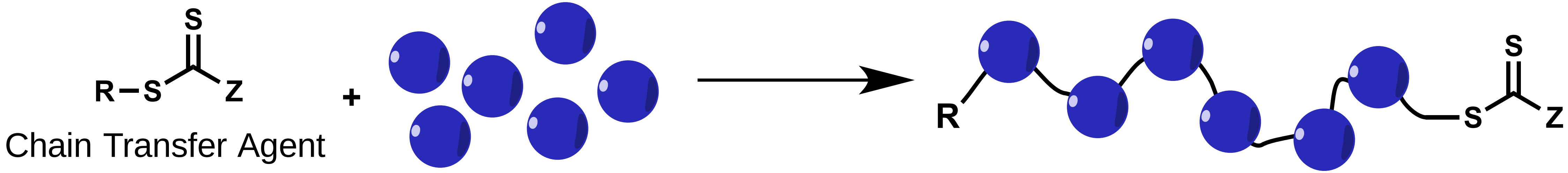
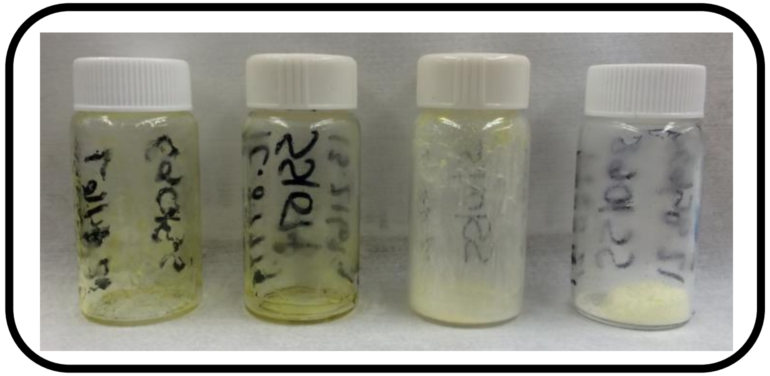
- Poor retention of chain end



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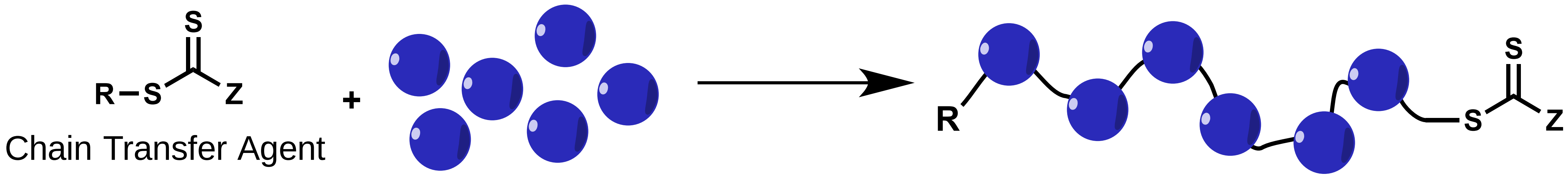
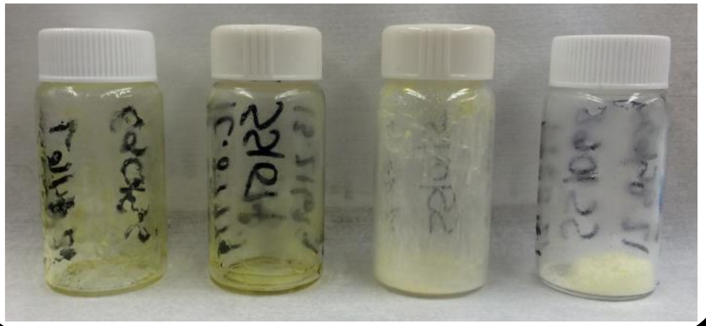
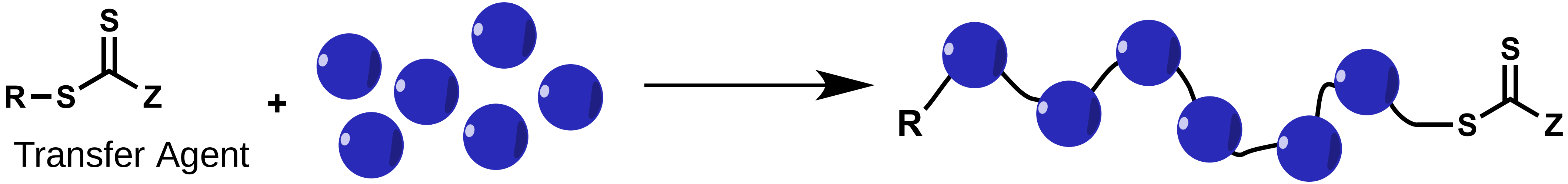
- Conjugation of chain end
  - Discoloration
- Poor retention of chain end
  - Odor

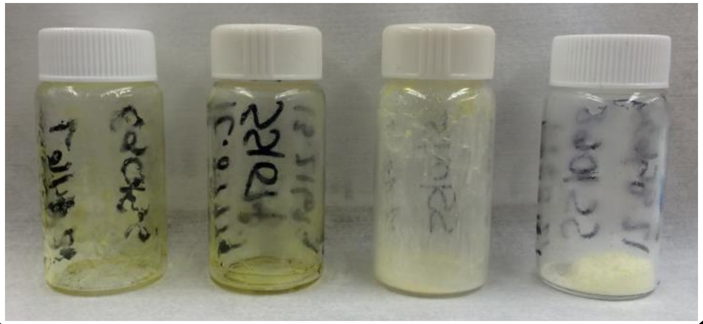


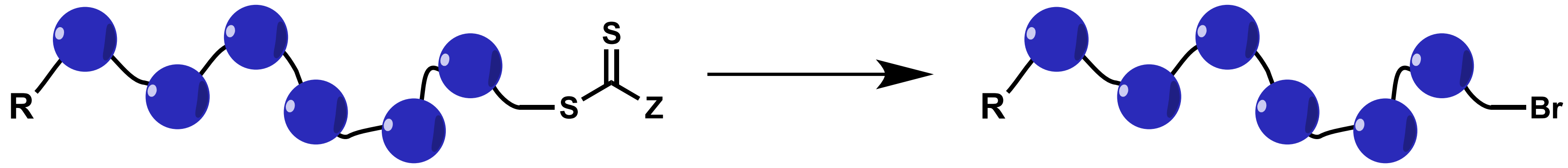
# Current Challenges with RAFT

- Conjugation of chain end
  - Discoloration
- Poor retention of chain end
  - Odor
  - Toxicity



# Functionalize RAFT Polymer Chain Ends with Bromides



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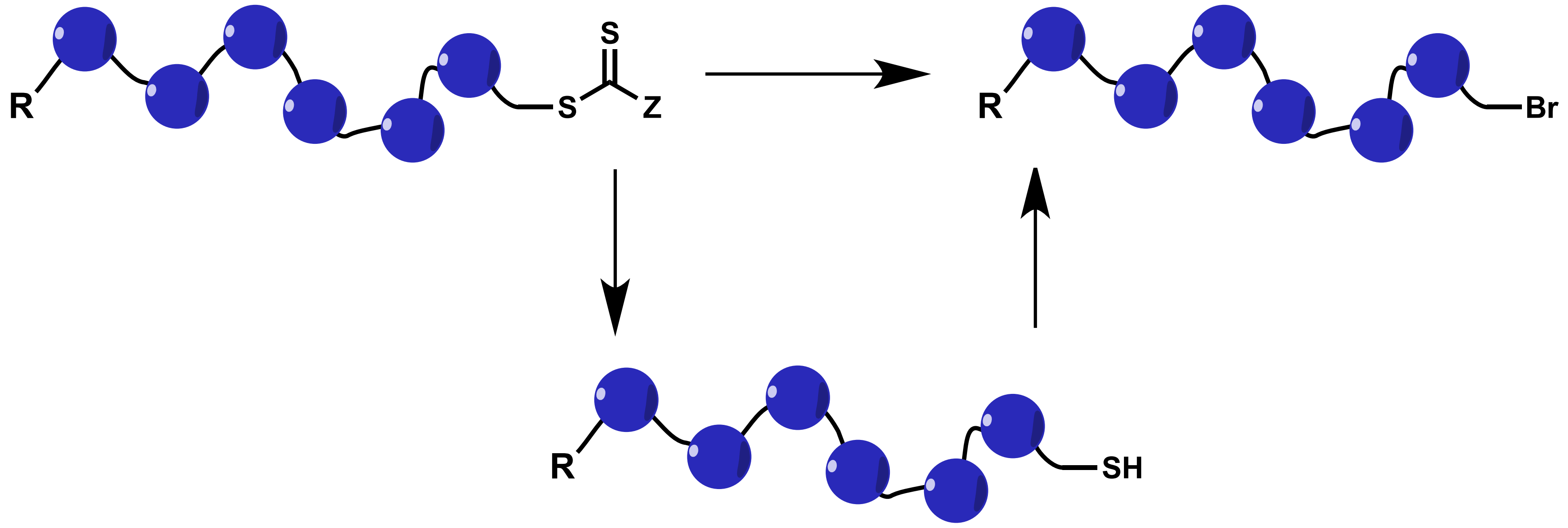

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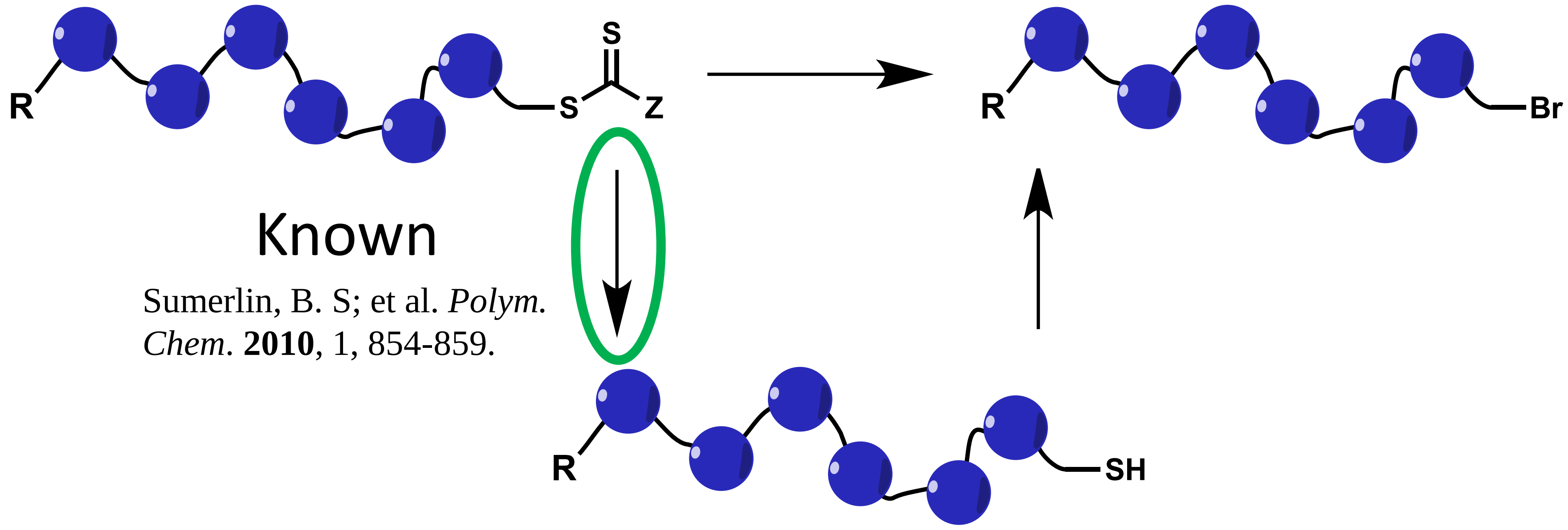


Known

Sumerlin, B. S; et al. *Polym. Chem*. **2010**, 1, 854-859.

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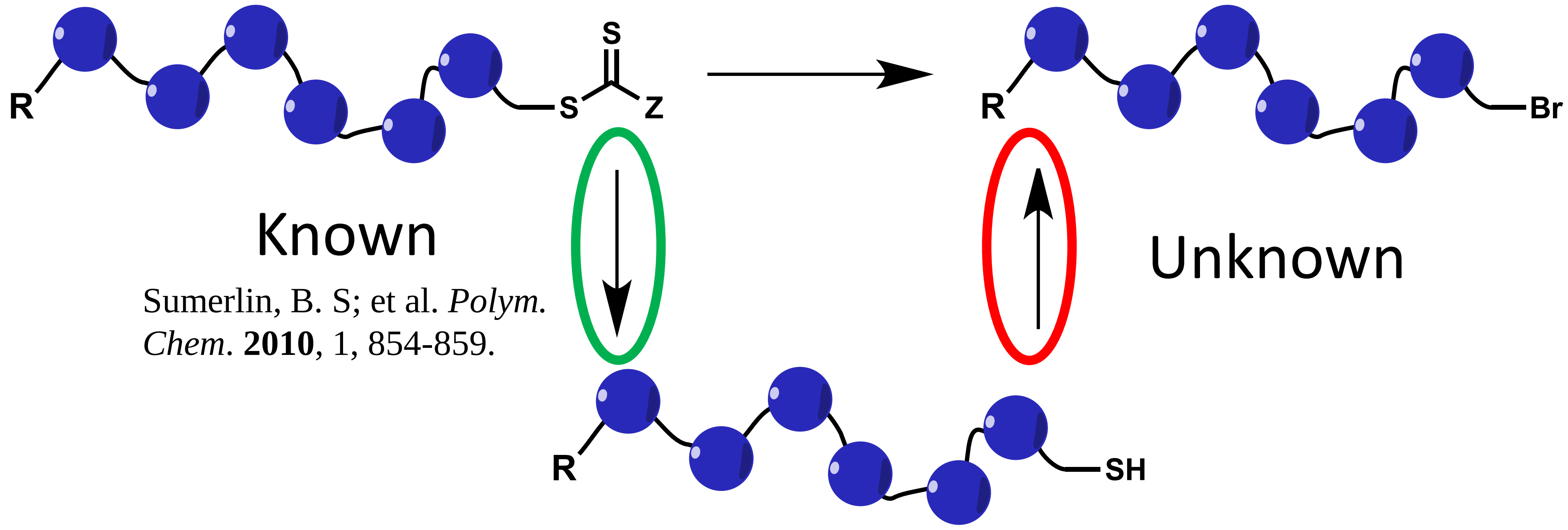


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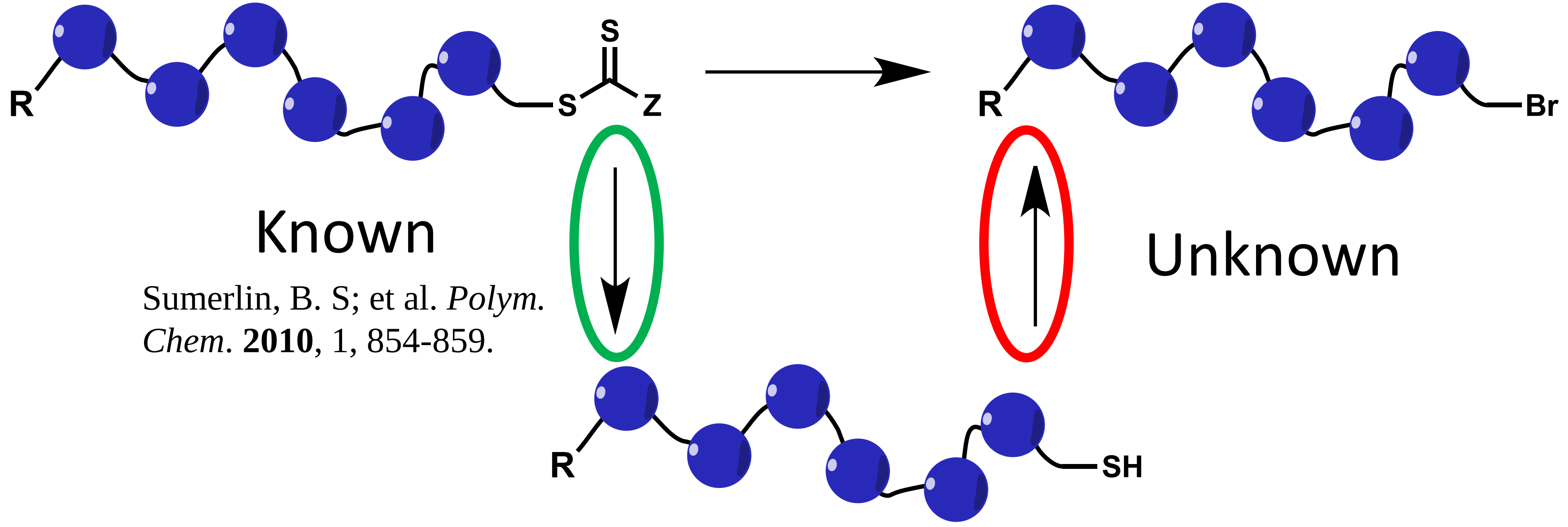


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Model Systems

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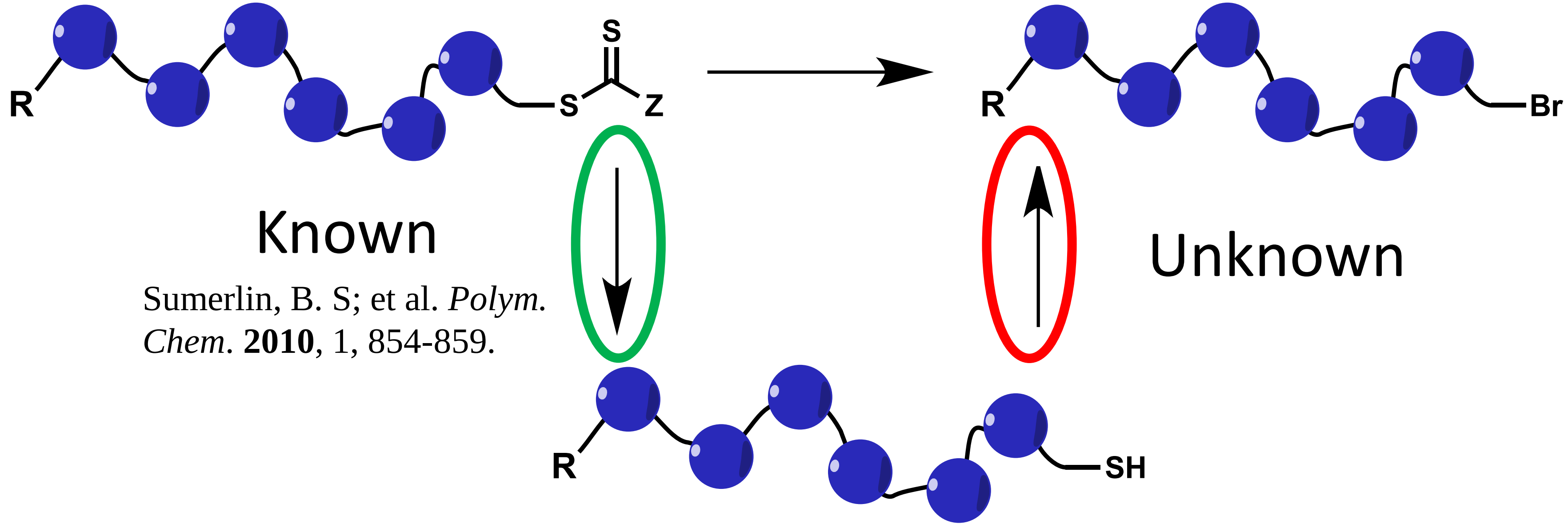


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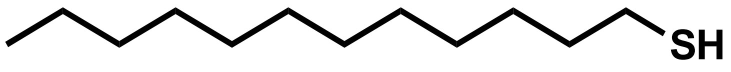


1-Dodecanethiol

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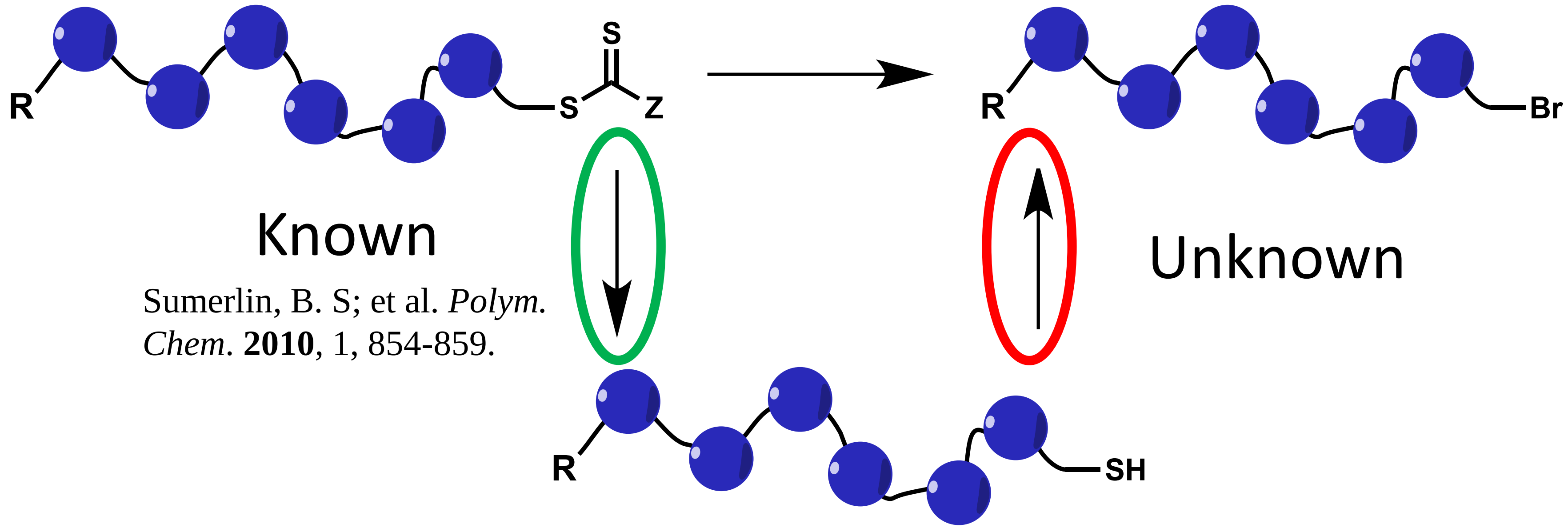
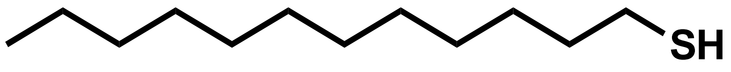



## Model Systems

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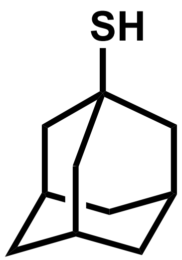


1-Adamantanethiol

# Setting Up the Reaction

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Reactants

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R–SH

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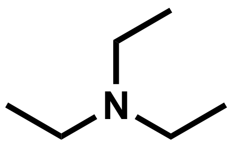
R–SH



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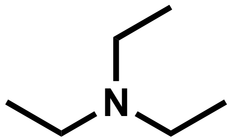


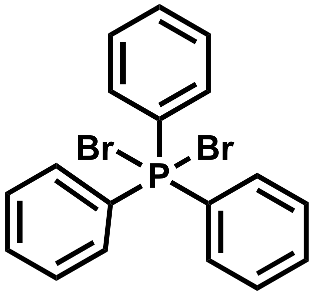

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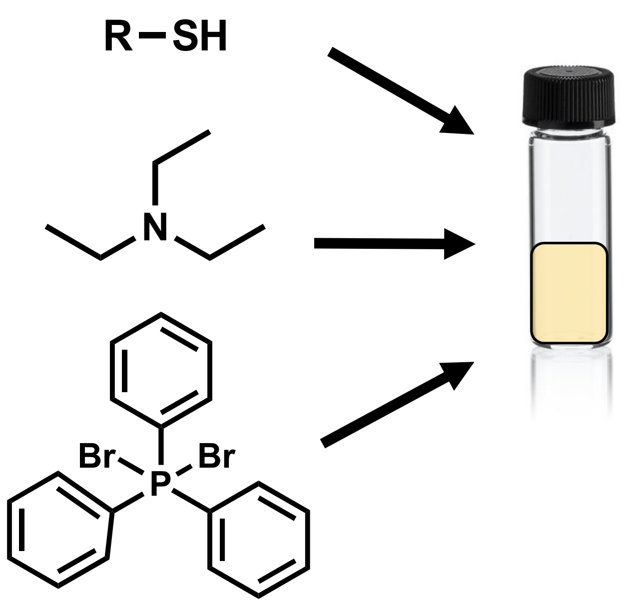

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# Setting Up the Reaction

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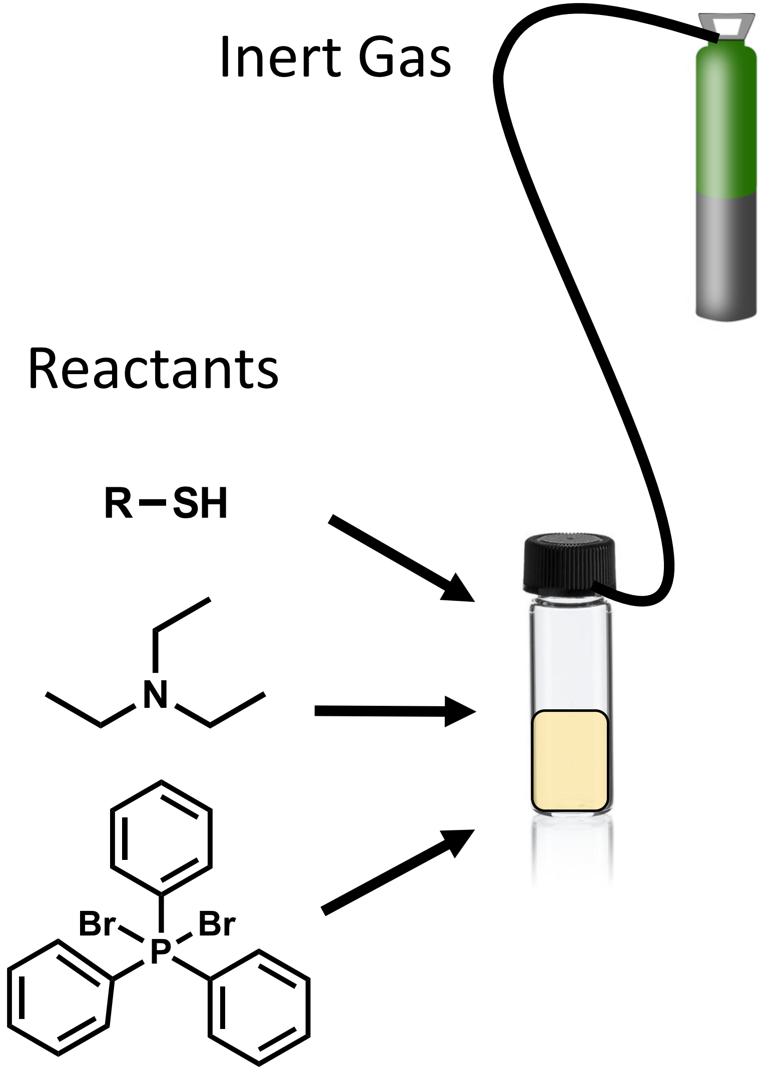

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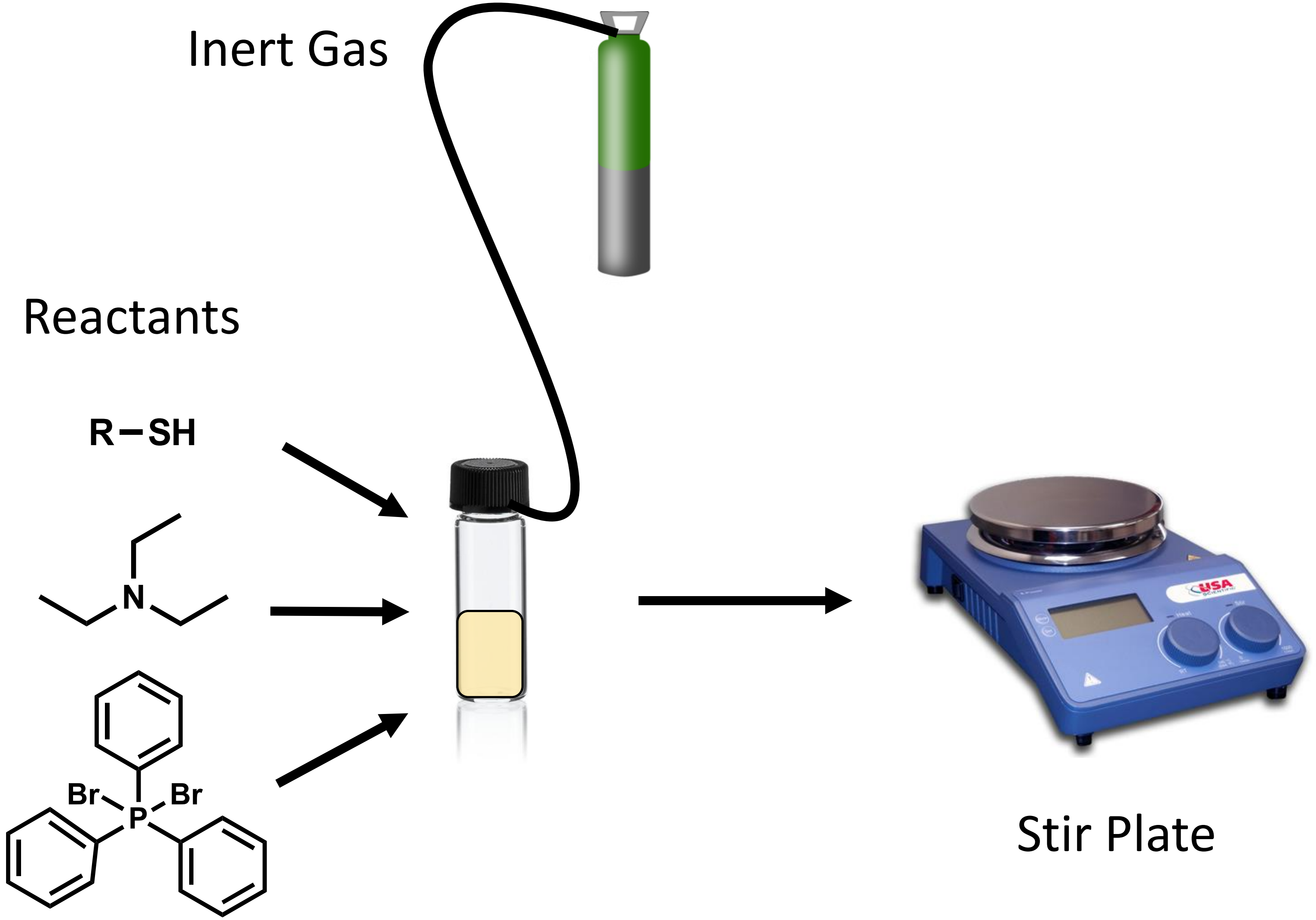

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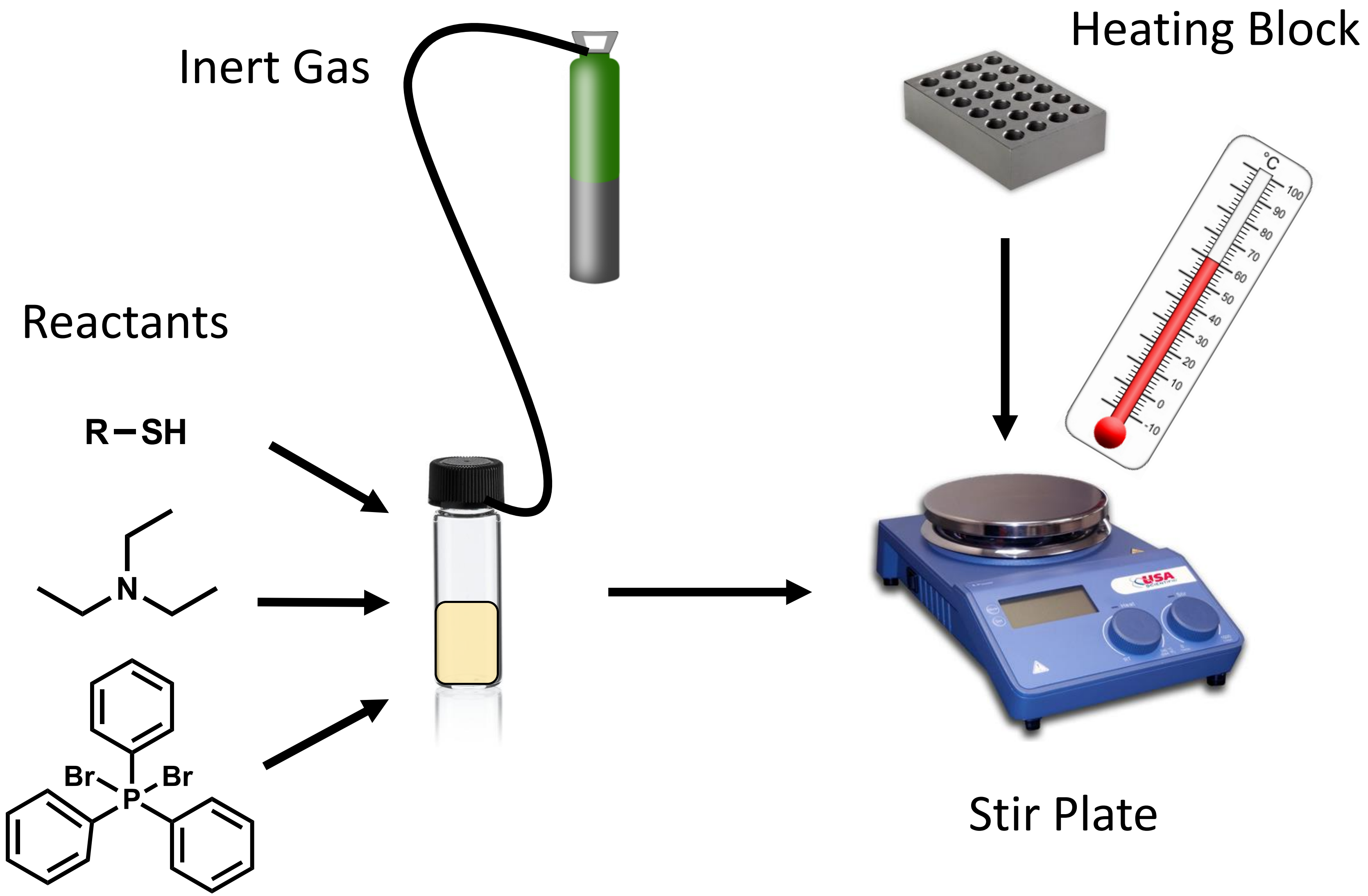

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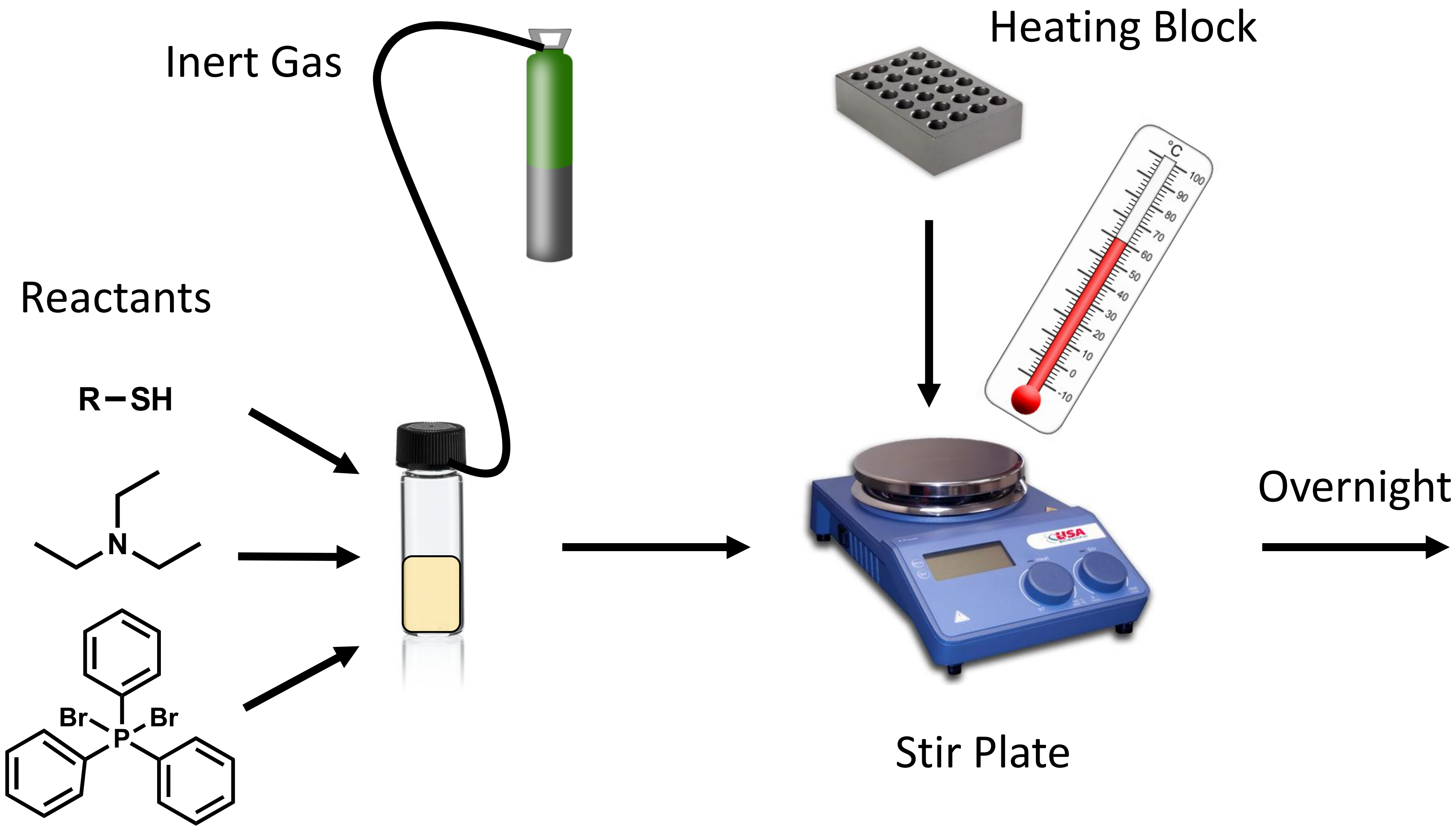

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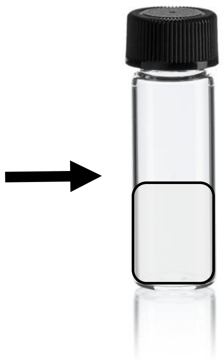

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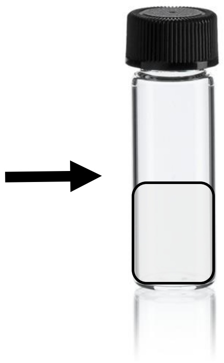
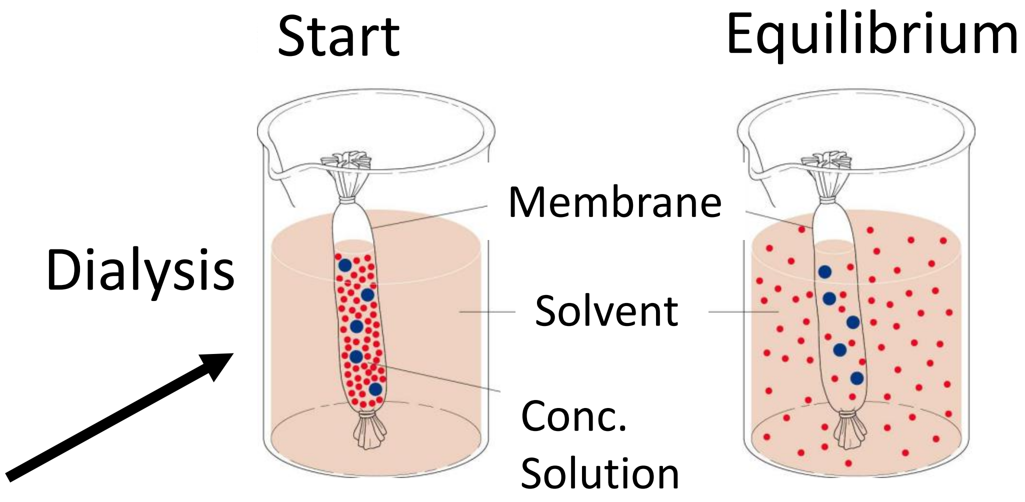


Dialysis



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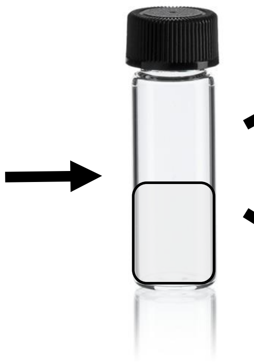
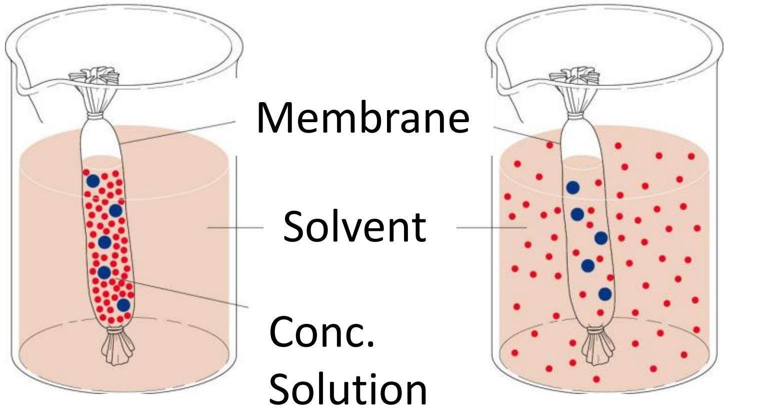


Dialysis

Start

Equilibrium




or

Precipitation

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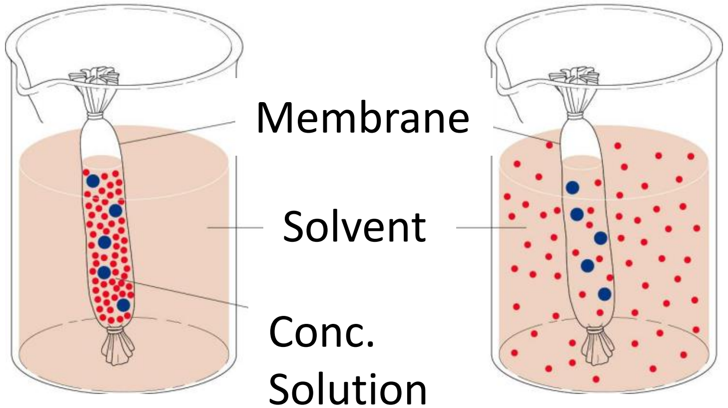


or

Precipitation

Remove
Solvent
Overnight

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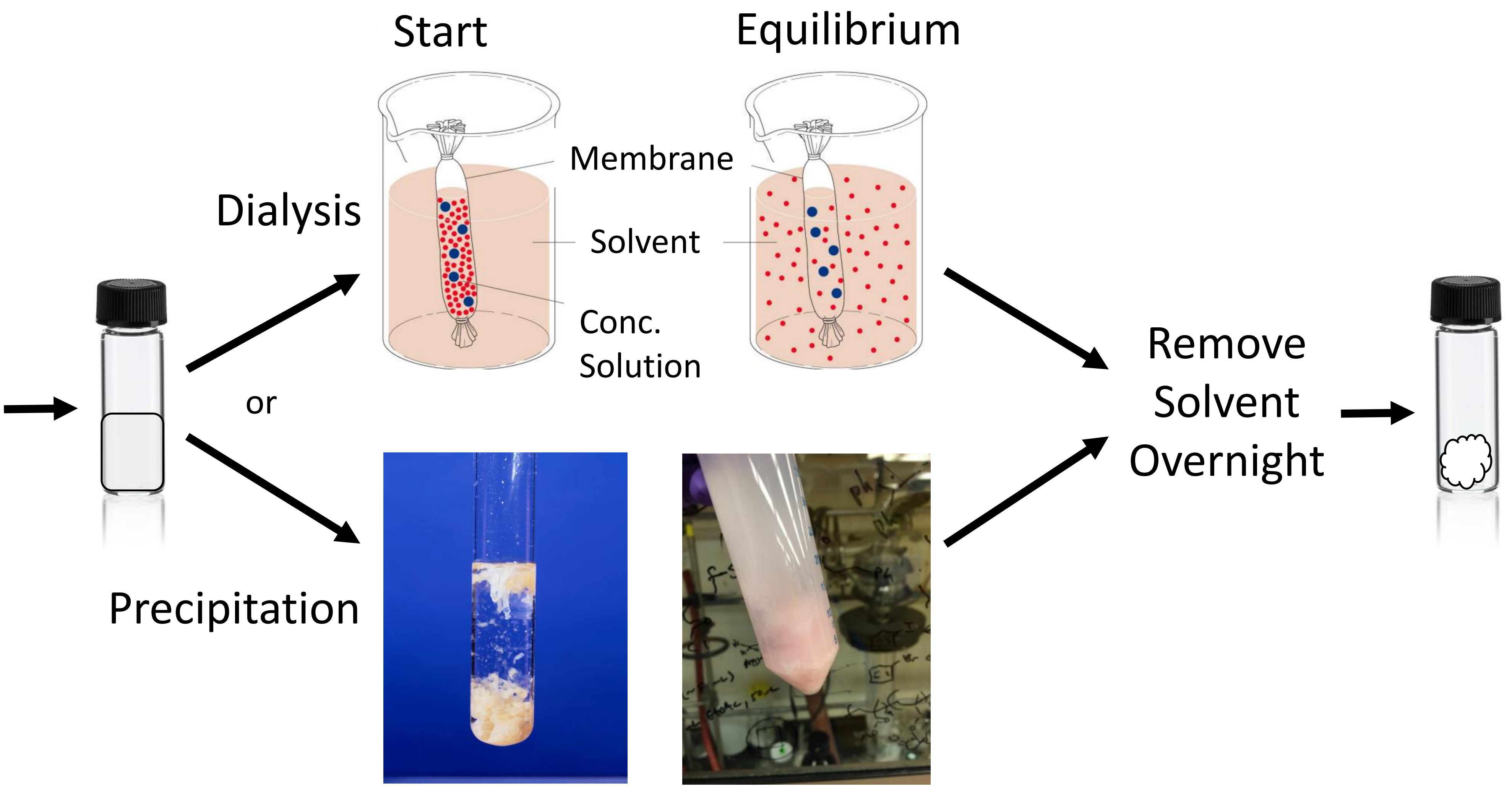

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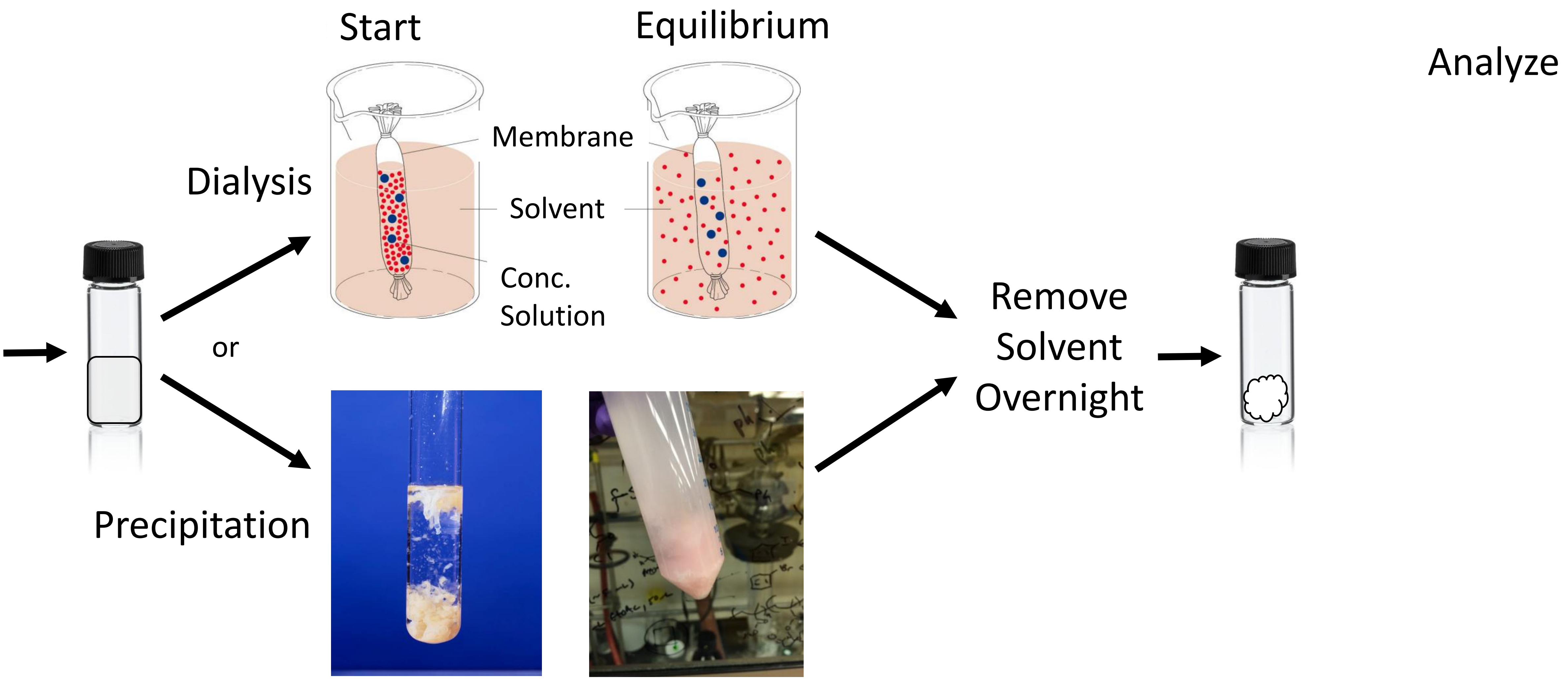

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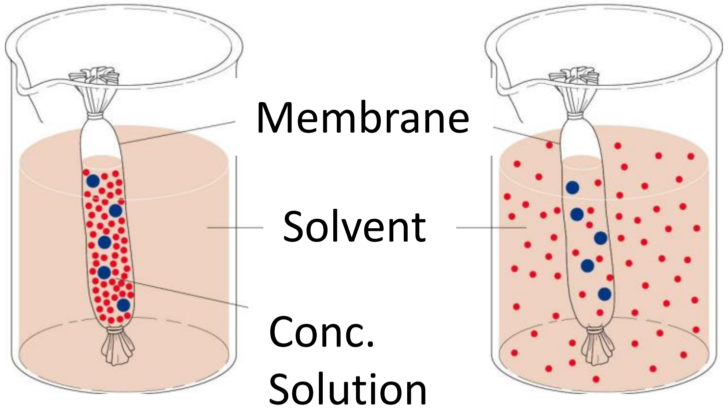



or

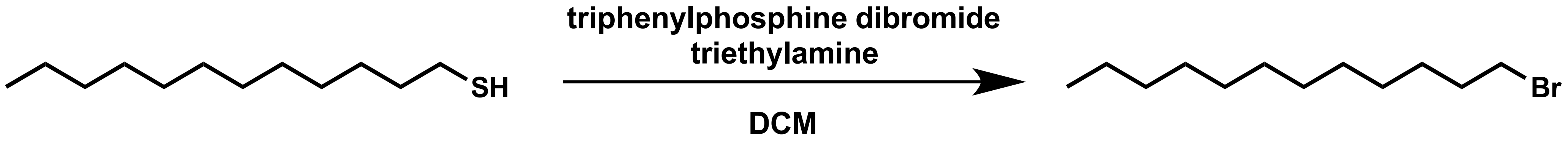
Precipitation

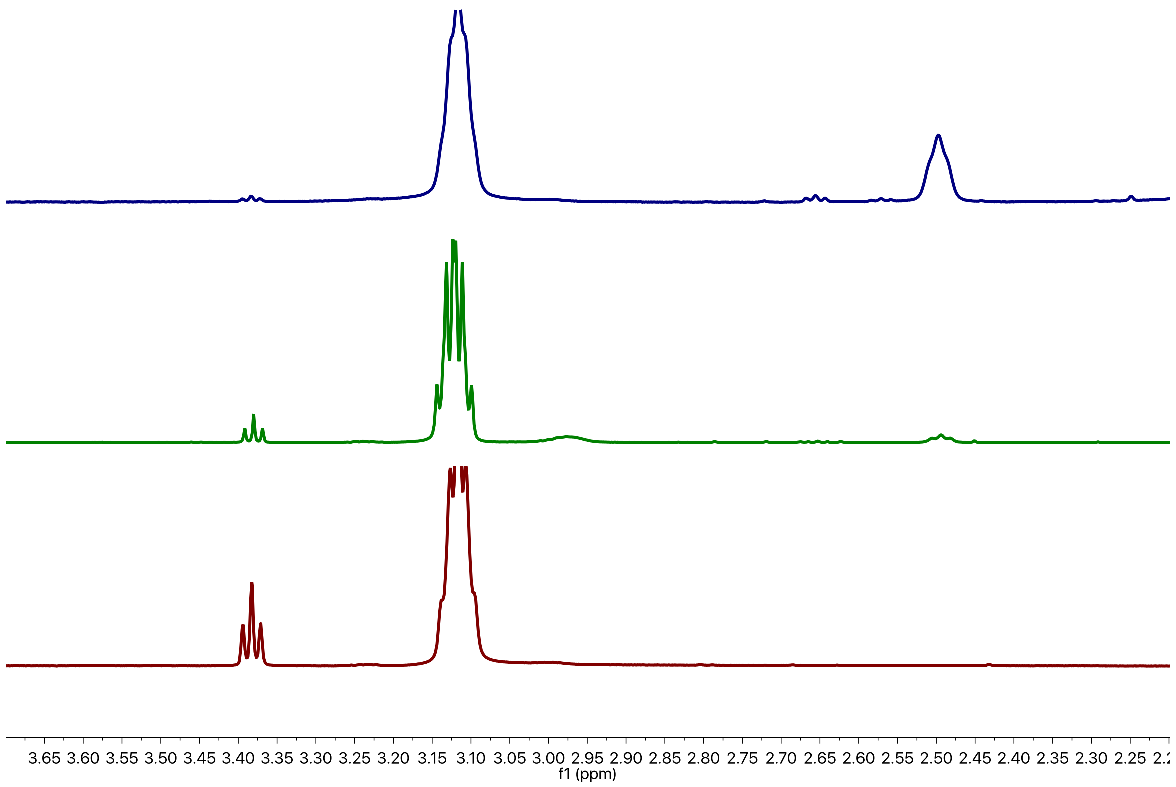
Remove Solvent Overnight

Analyze

Nuclear Magnetic Resonance (NMR) Spectroscopy

# Model System: Dodecanethiol




Starting material

56% conversion

>99% conversion

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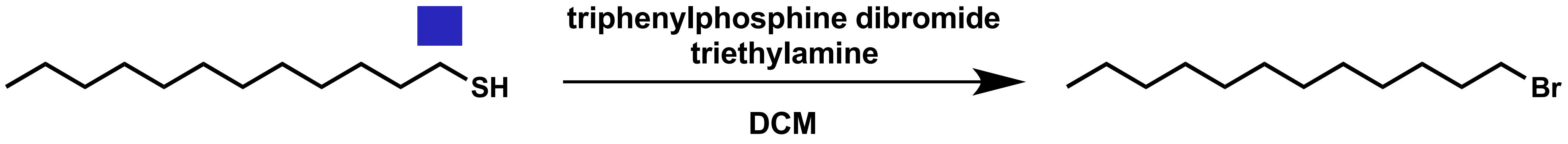


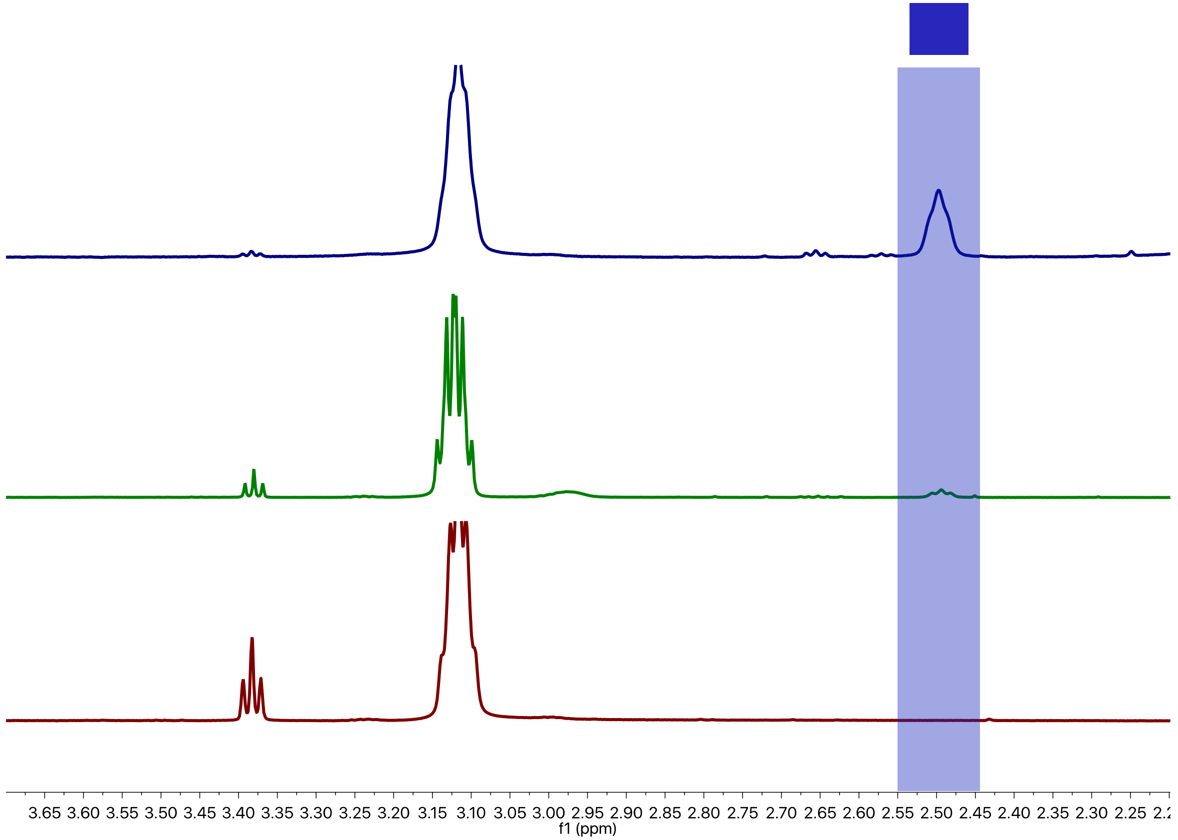


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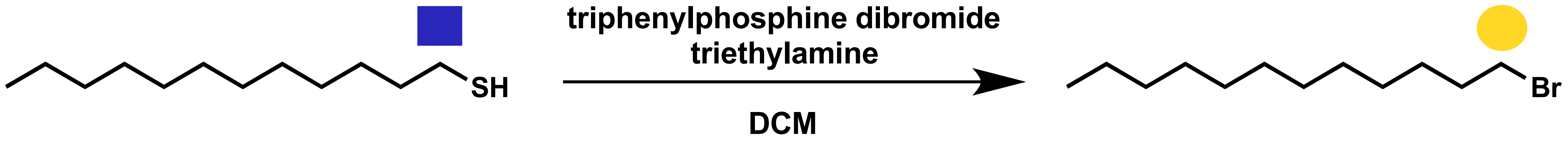


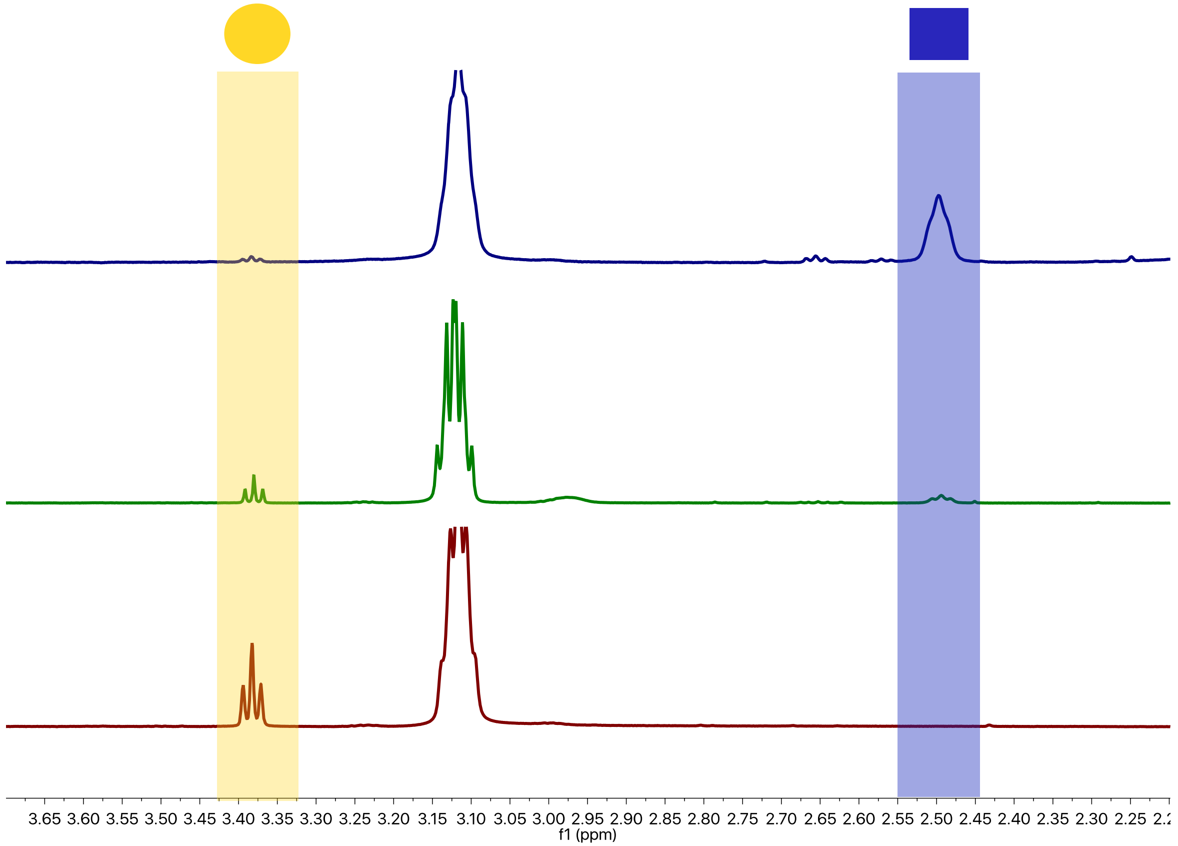

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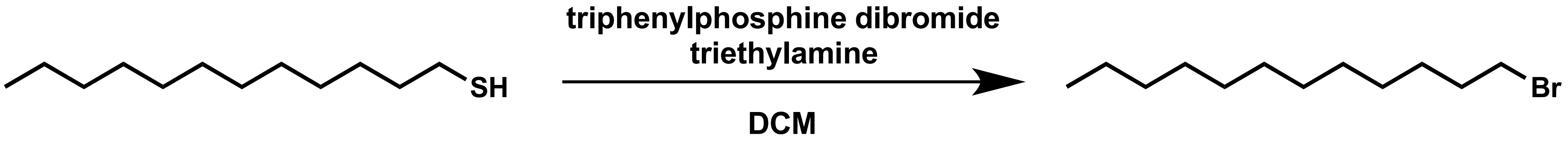
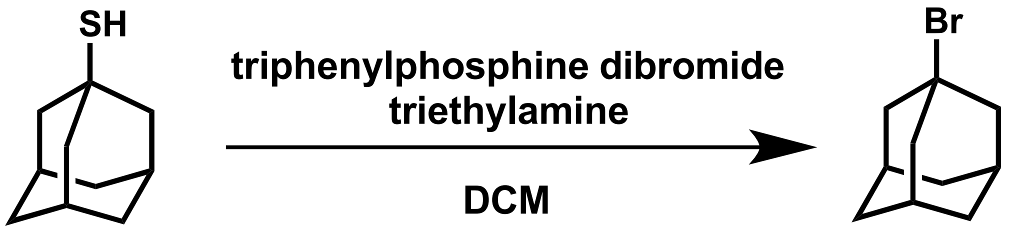
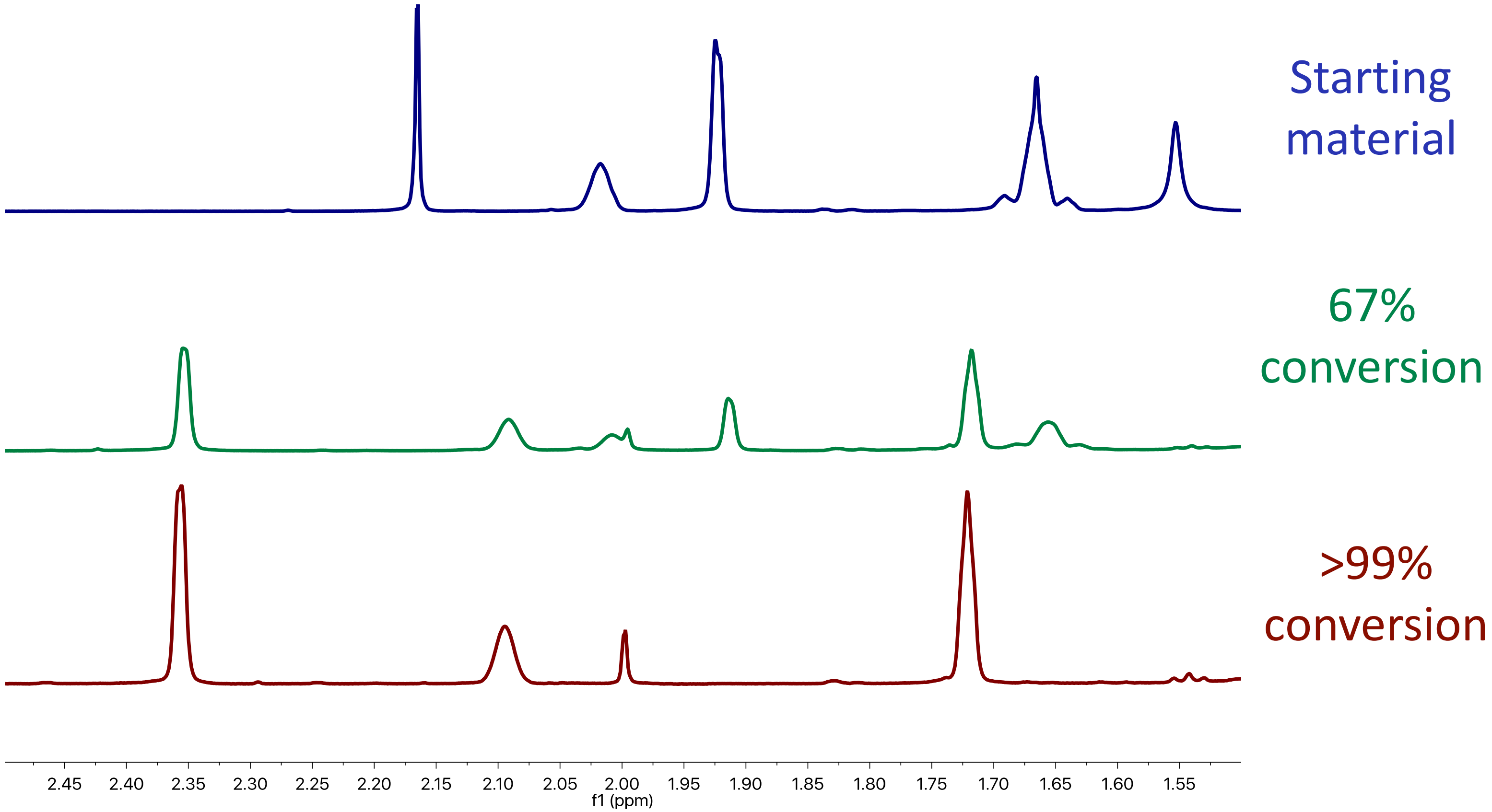



| Eqv. Dodecanethiol | Eqv. Triphenylphosphine dibromide | Eqv. Triethylamine | Solvent | Sparged with argon? | Temp. (°C) | Time (hr) | Conversion |
|---|---|---|---|---|---|---|---|
| 1.00 | 3.00 | 3.00 | DCM | yes | room | 18 | >99% |

*Conversion determined by $^{1}$H-NMR

# Model System: Adamantanethiol



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# Model System: Adamantanethiol

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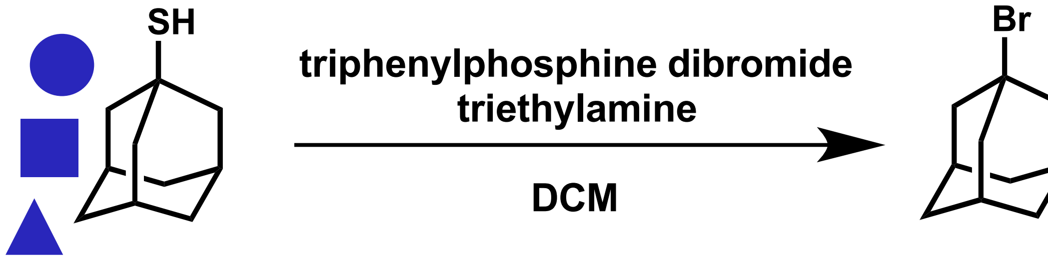
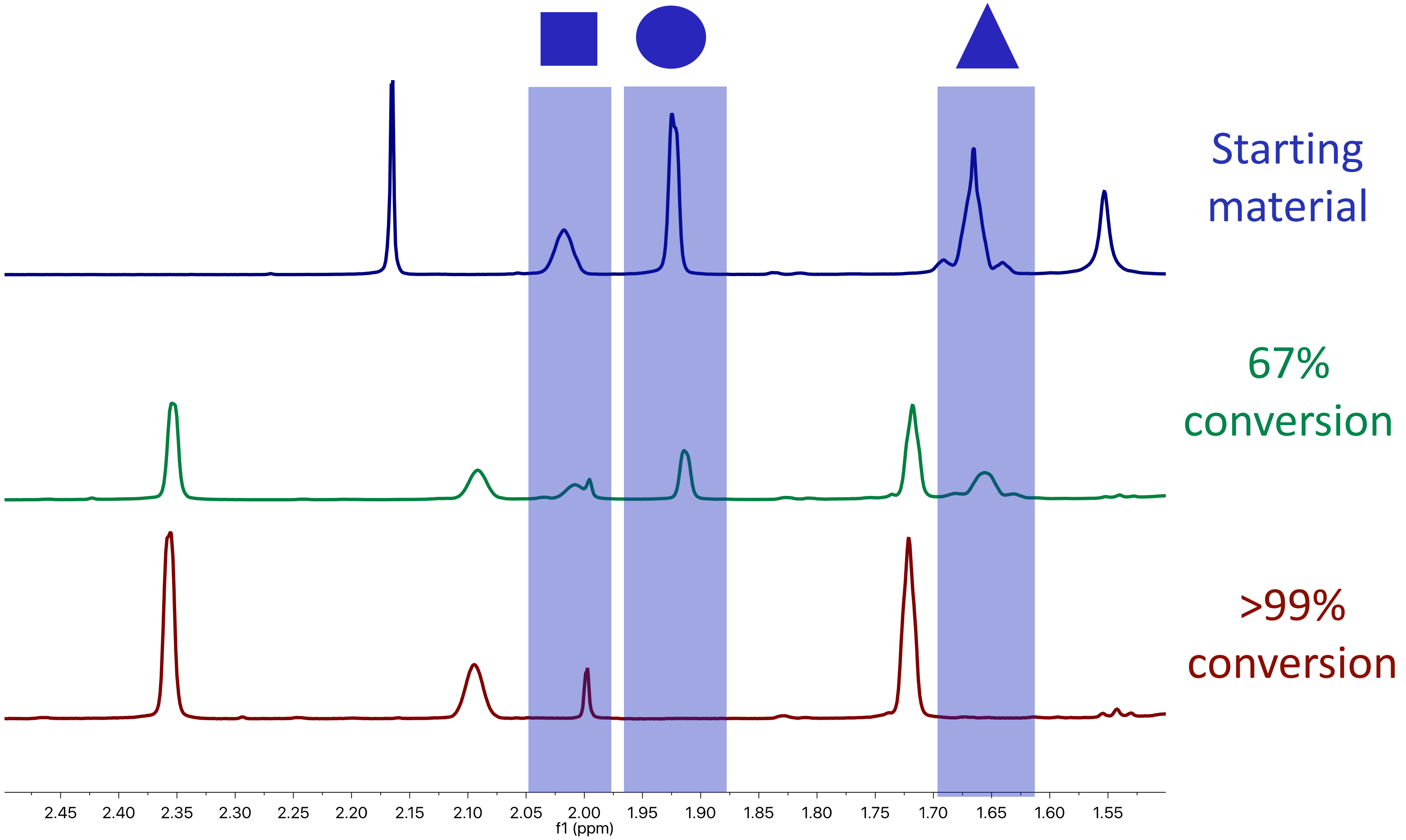
National Institutes of Health



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# Model System: Adamantanethiol

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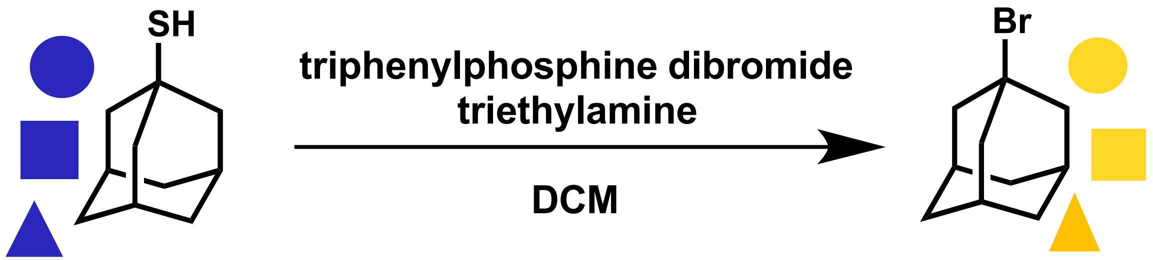
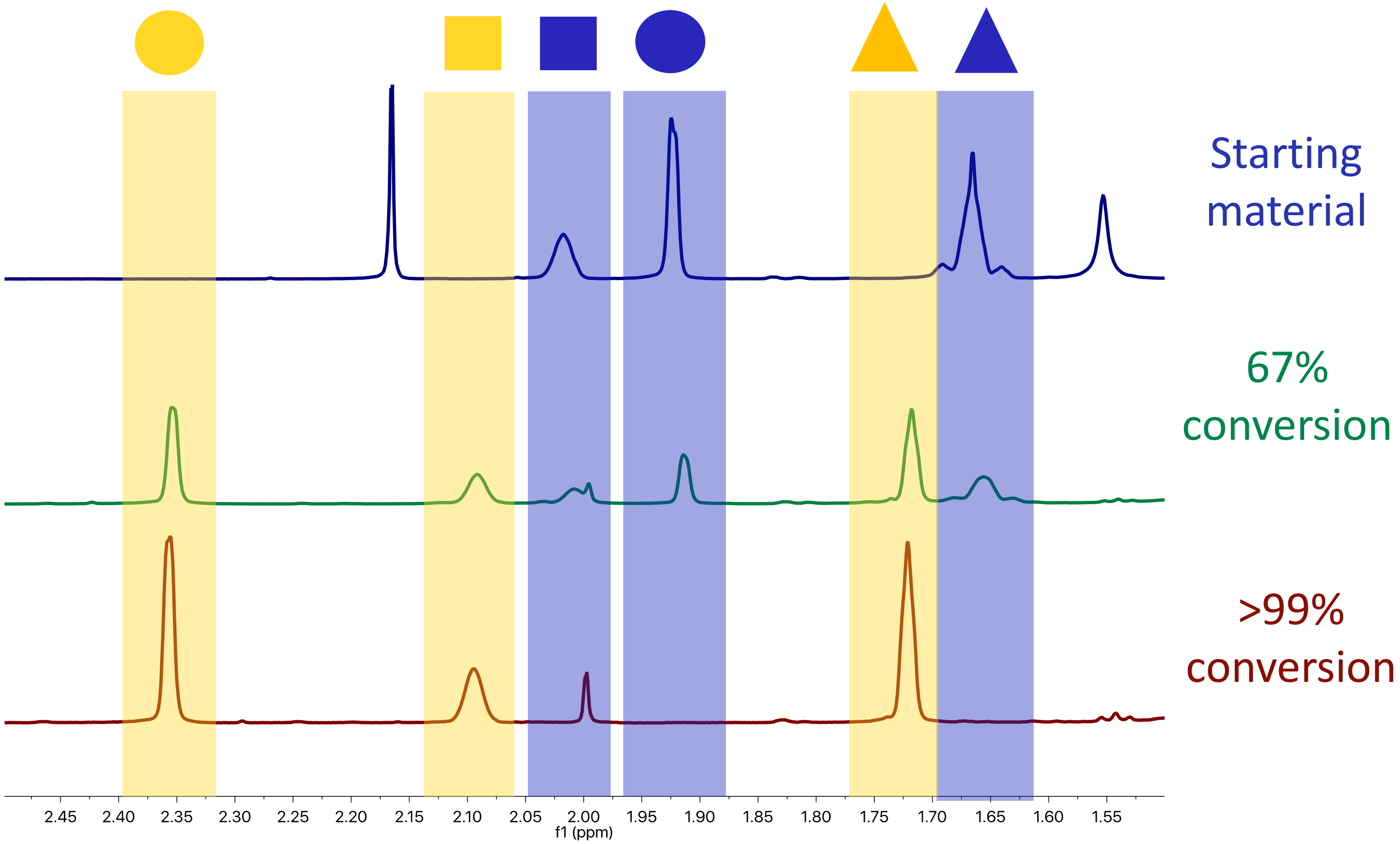
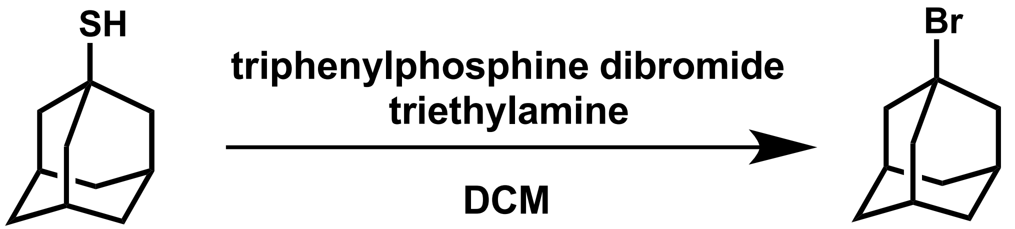


# Model System: Adamantanethiol




| Eqv. Adamantanethiol | Eqv. Triphenylphosphine dibromide | Eqv. Triethylamine | Solvent | Sparged with argon? | Temp. (℃) | Time (hr) | Conversion |
|---|---|---|---|---|---|---|---|
| 1.00 | 5.00 | 5.00 | DCM | yes | 45 | 5 | 100% |
| 1.00 | 5.00 | 5.00 | DCM | yes | room | 5 | 85% |
| 1.00 | 10.00 | 10.00 | DCM | yes | 45 | 26 | 100% |

*All conversions determined by H-NMR

# Bromination on Polymers

# Bromination on Polymers

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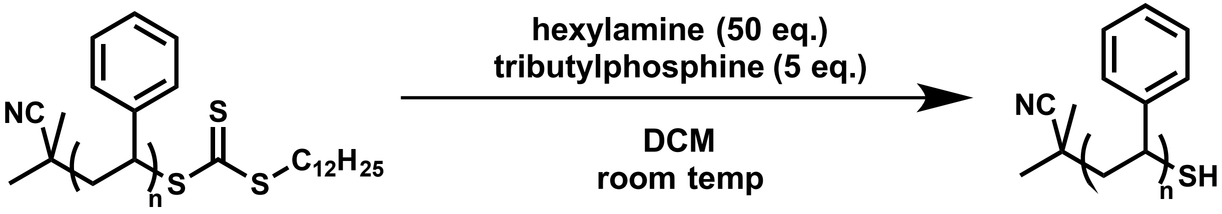
## Polystyrene

In-Hwan Lee

# Bromination on Polymers

## Polystyrene

In-Hwan Lee



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# Bromination on Polymers

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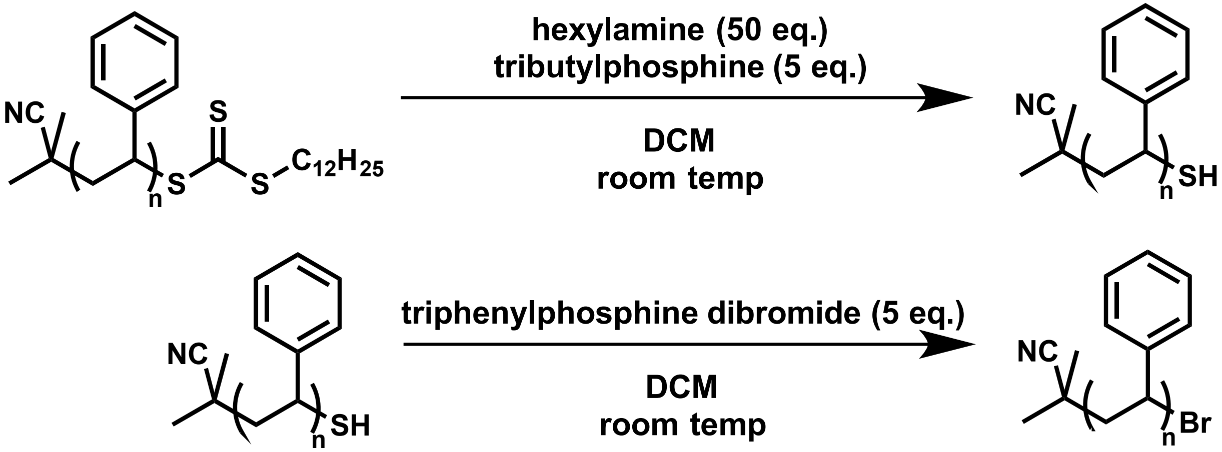
## Polystyrene

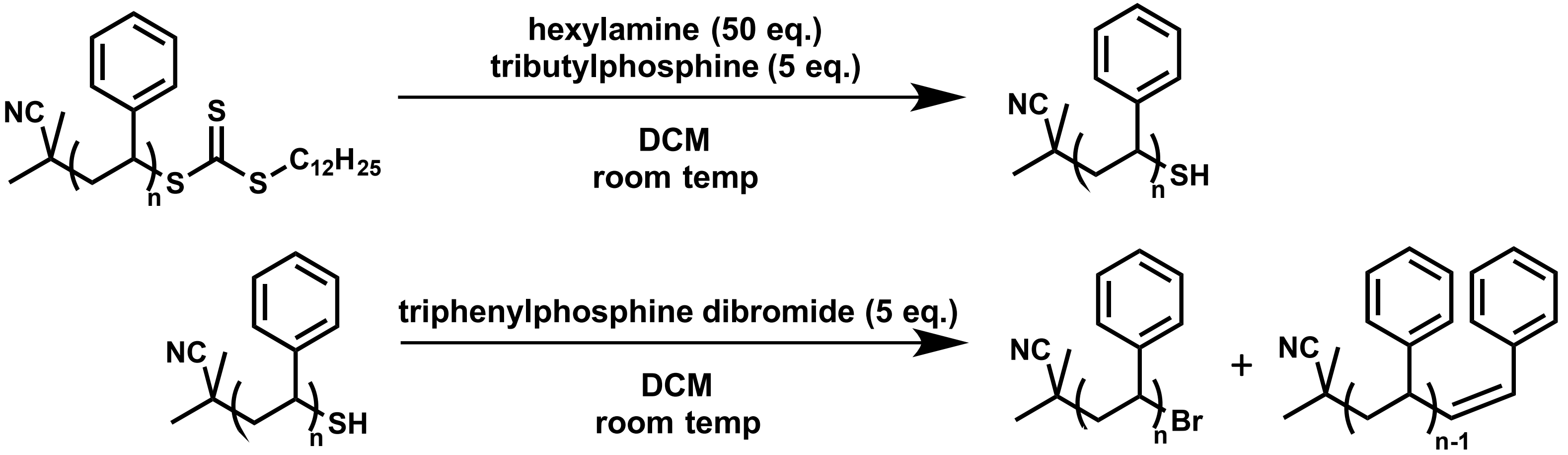
In-Hwan Lee



# Bromination on Polymers

## Polystyrene

In-Hwan Lee




2:1

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# Bromination on Polymers

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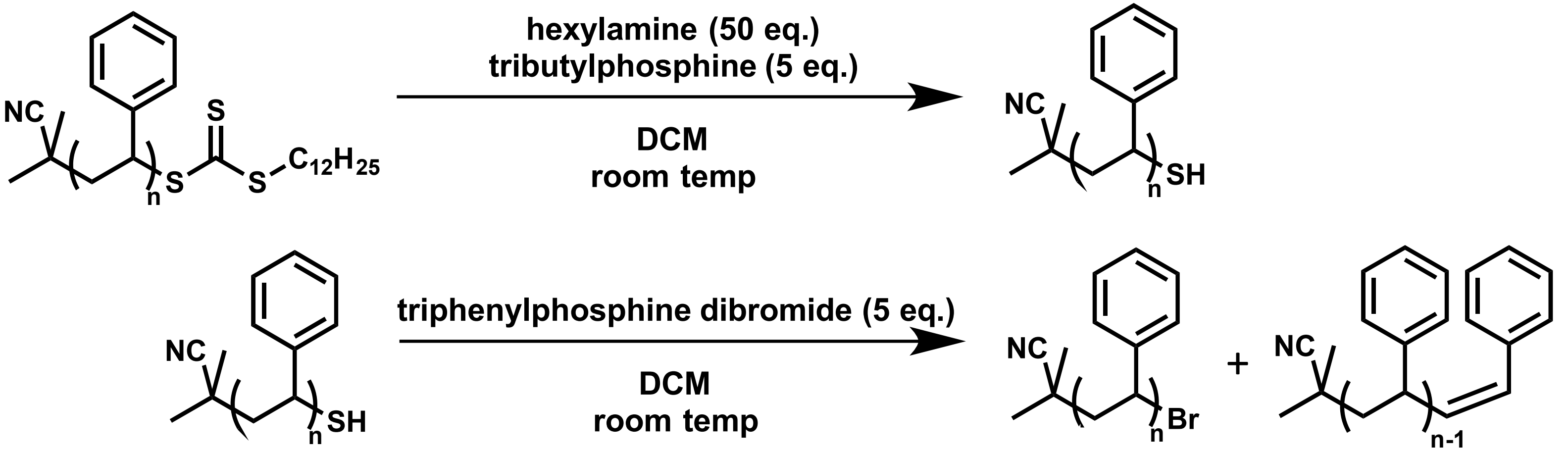
## Polystyrene

In-Hwan Lee




2:1

## Poly(methyl acrylate)

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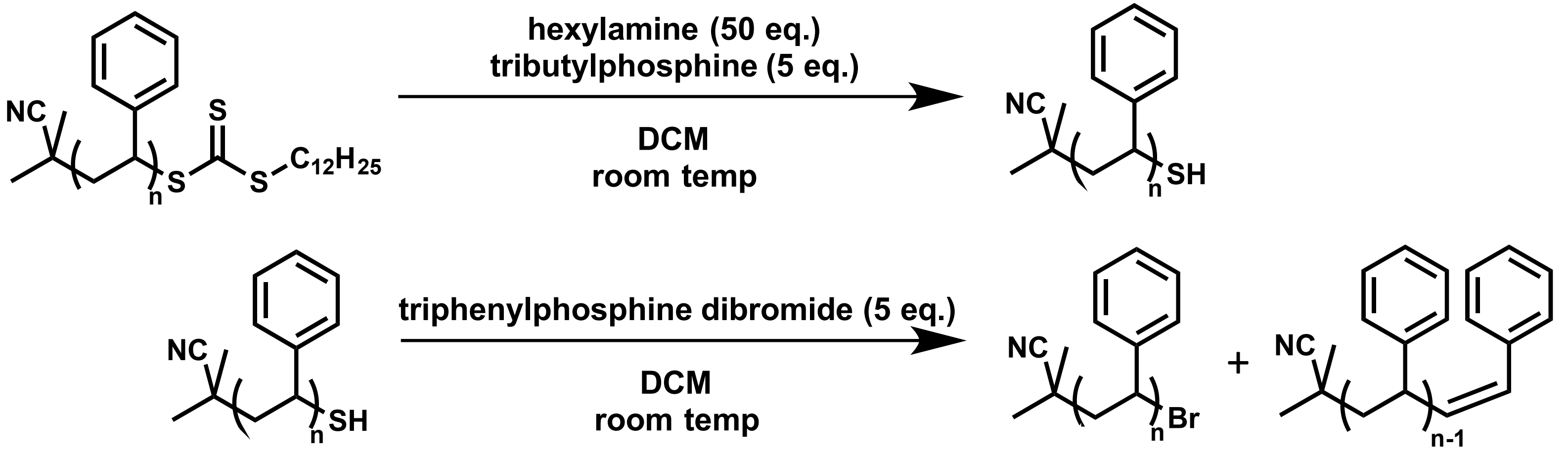
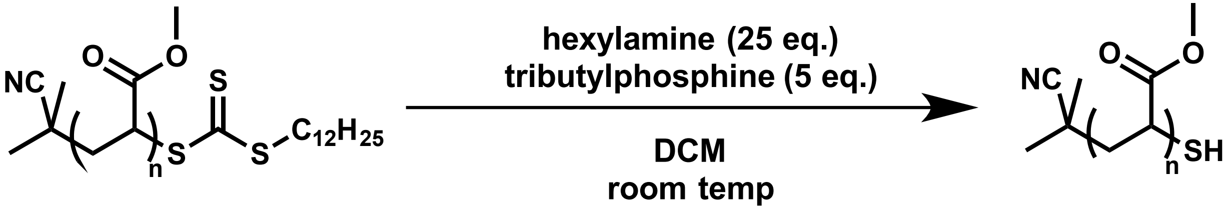
## Polystyrene

In-Hwan Lee




2:1

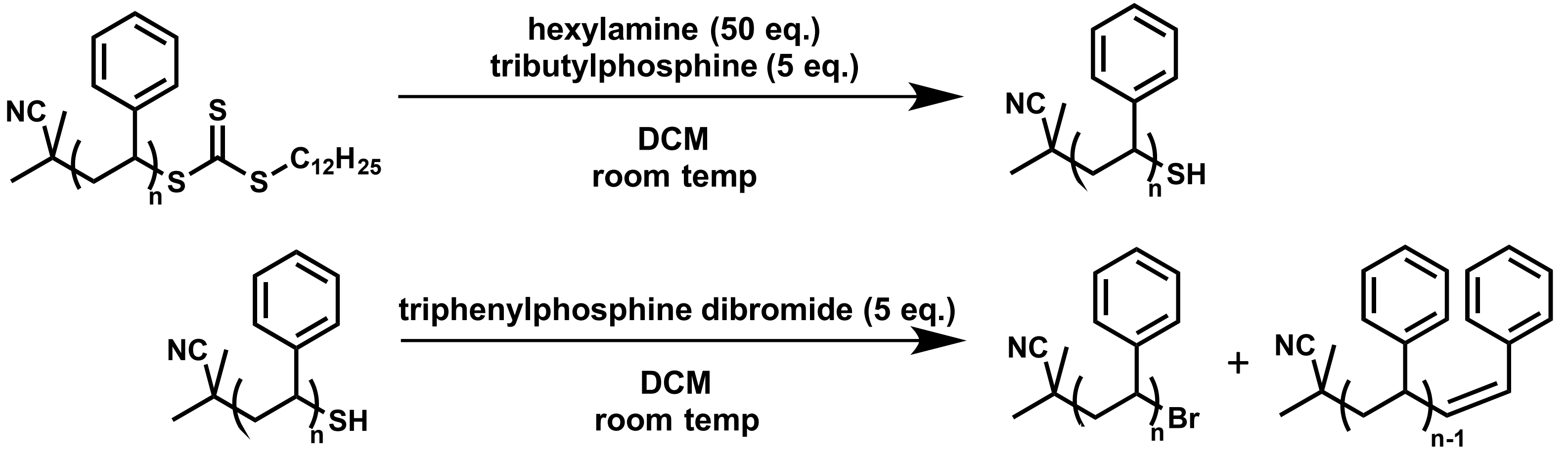
## Poly(methyl acrylate)



# Bromination on Polymers

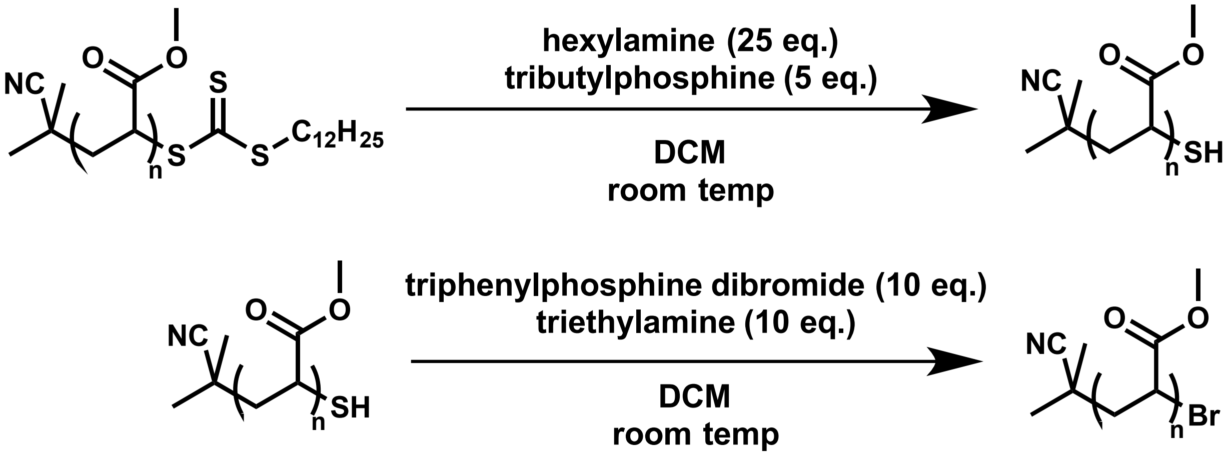
## Polystyrene

In-Hwan Lee




2:1

## Poly(methyl acrylate)



# Bromination on Polymers

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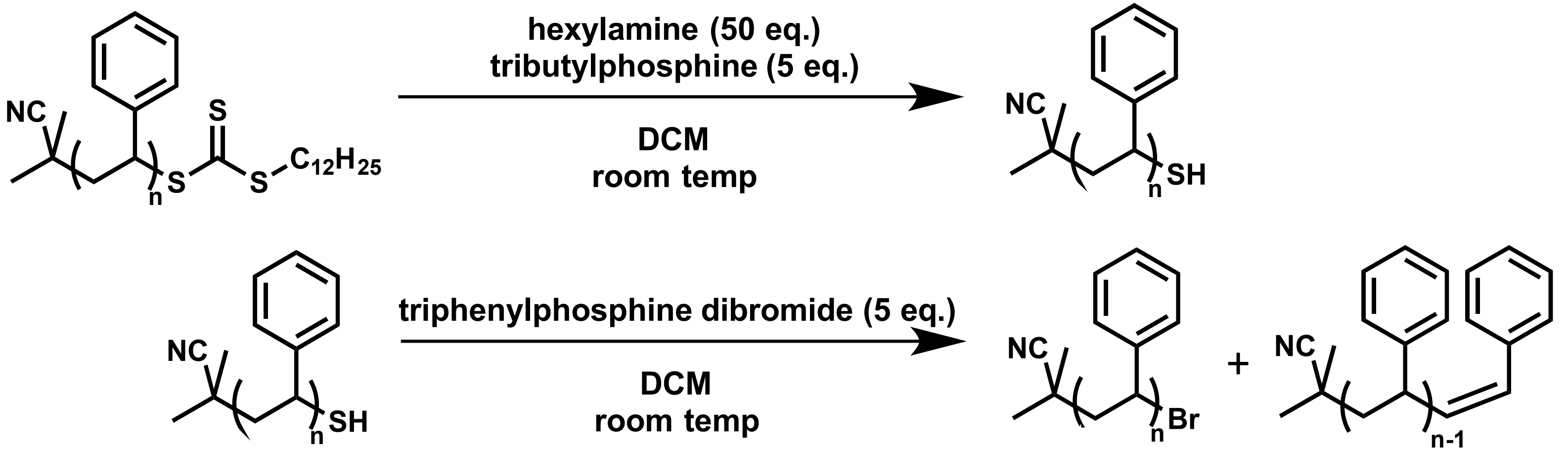
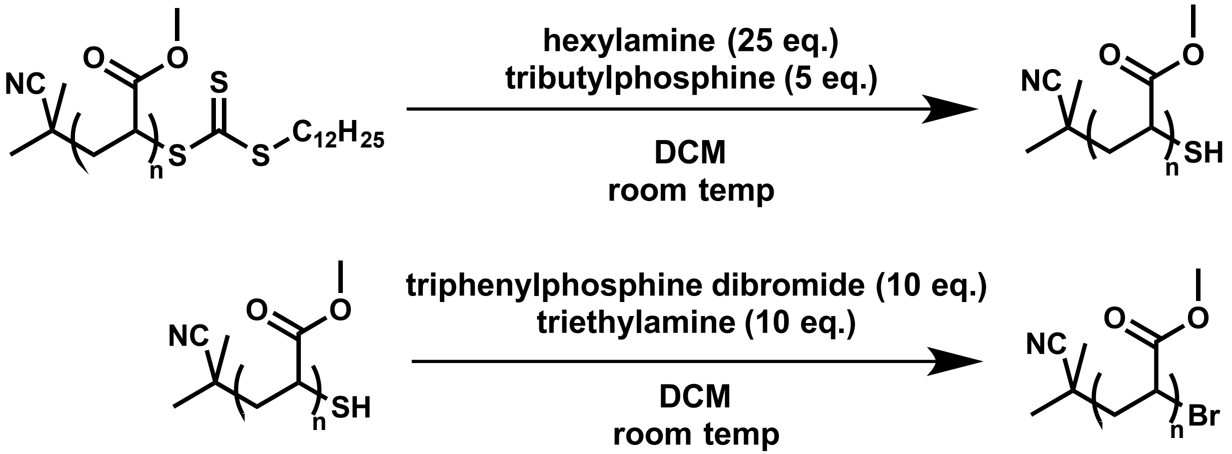
## Polystyrene

In-Hwan Lee



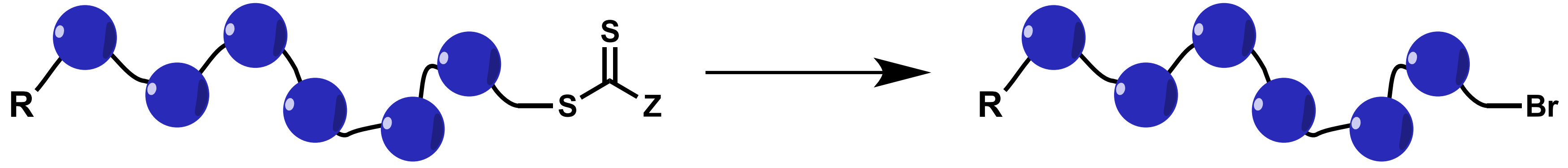

2:1

## Poly(methyl acrylate)




Not complete conversion

# Future Work: Further Optimization on Polymers Systems




- Solvent
- Temperature
- Equivalents
- Reagents

# Thank you!

## The Read de Alaniz Group:

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Andre St. Amant
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Landon Mills
Joseph Sanz

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