# Literature Report V

# The Synthesis of Poly(thioether)s via oxygen/sulfur exchange reactions

**Reporter: Xiao-Qing Wang**
**Checker: Yi-Xuan Ding**
**Date: 2020-07-13**

Zhang, X.-H. et al. *Macromolecules* **2020**, *53*, 233.
Zhang, X.-H. et al. *J. Am. Chem. Soc.* **2019**, *141*, 5490.

# CV of Xing-Hong Zhang

## Education:

- **1996–2000** B.S., Fuyang Normal University
- **2000–2003** M.S., Shantou University
- **2003–2006** Ph.D., Zhejiang University
- **2006–2009** Associate Professor, Zhejiang University
- **2009–Present** Professor, Zhejiang University

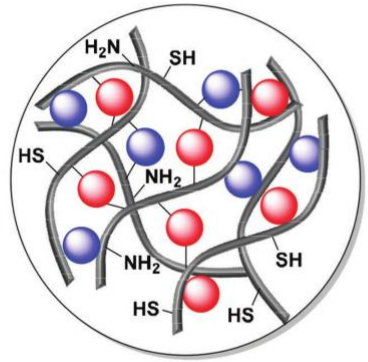
## Research:

- Polymer Chemistry and Functional Materials

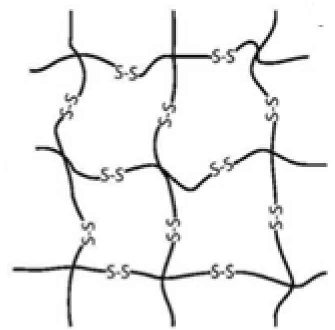
# Contents

# Introduction

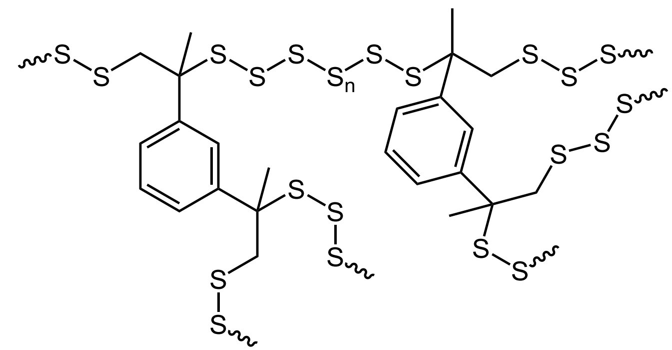
*Applications of sulfur-polymers and materials*



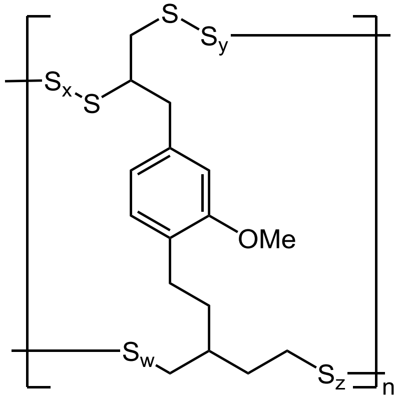

Hydrogels



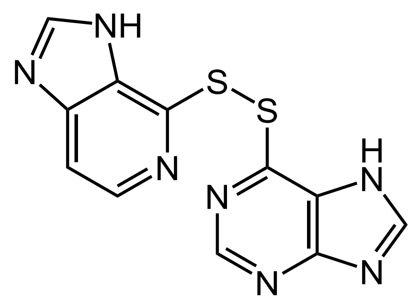

Self-Healing




Metal-Ion Removal



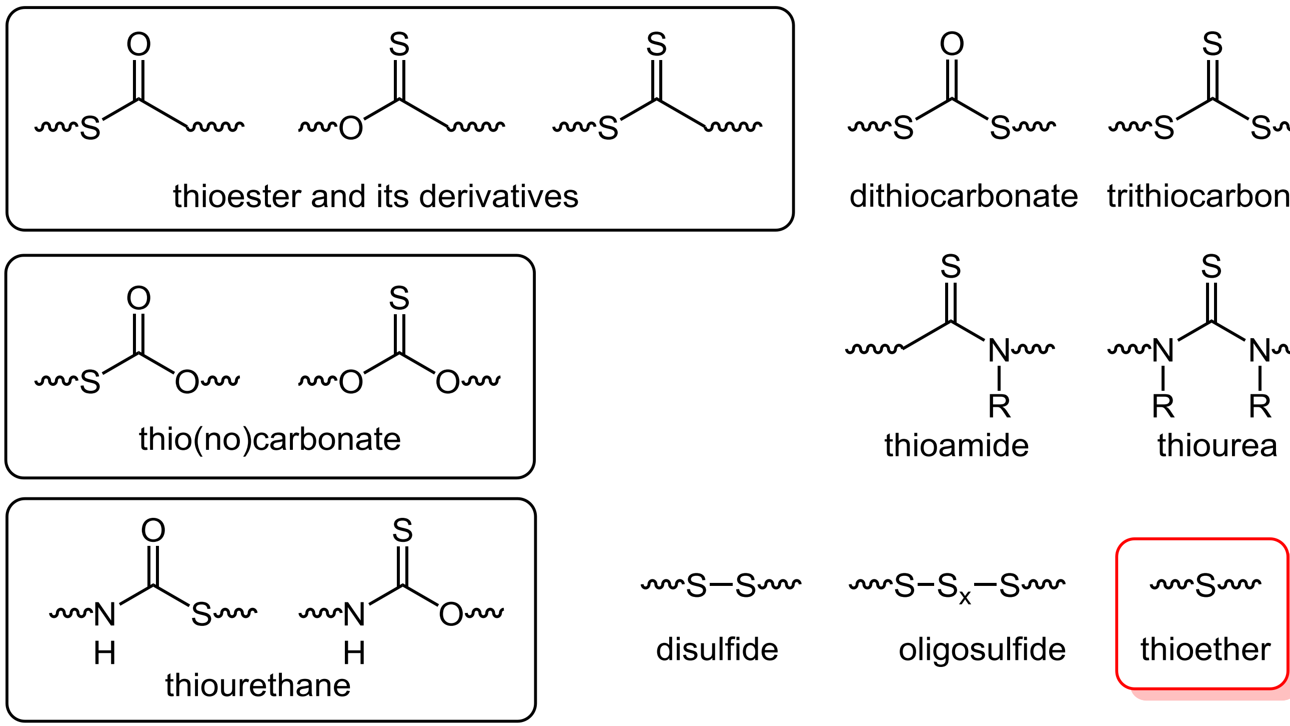

Energy Storage




Drug-Delivery

# Introduction

*Polymers possessing the depicted sulfur functional groups*

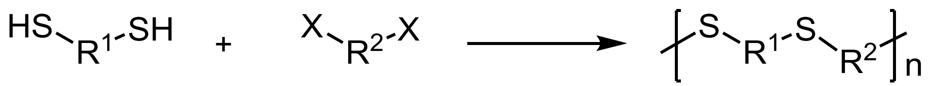



Theato, P. et al. *Macromol. Rapid Commun.* **2019**, *40*, 1800650.

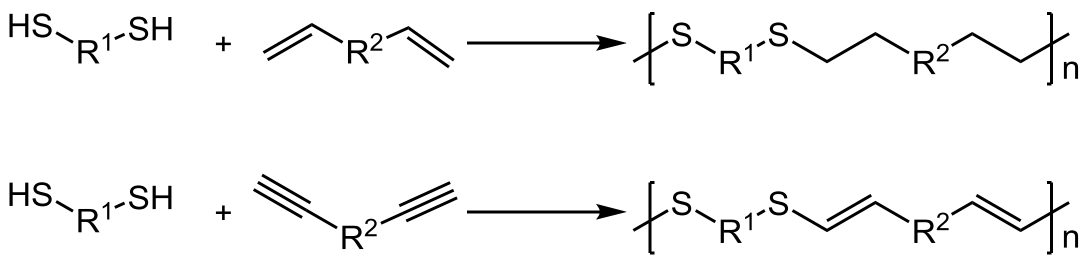
# Introduction

*Representative methods for the synthesis of poly(thioether)s*

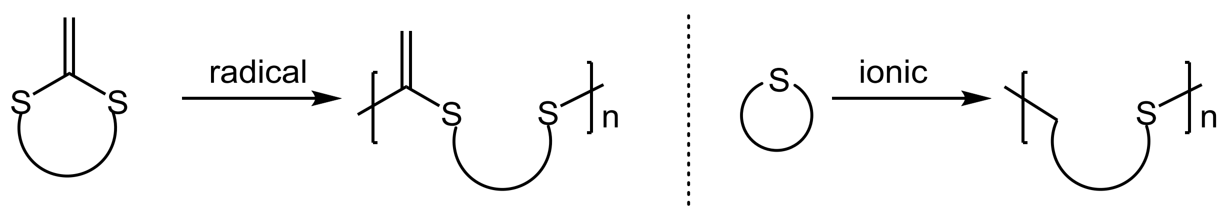
***1. The nucleophilic substitution reaction***




***2. The thiol-ene/yne addition reaction***

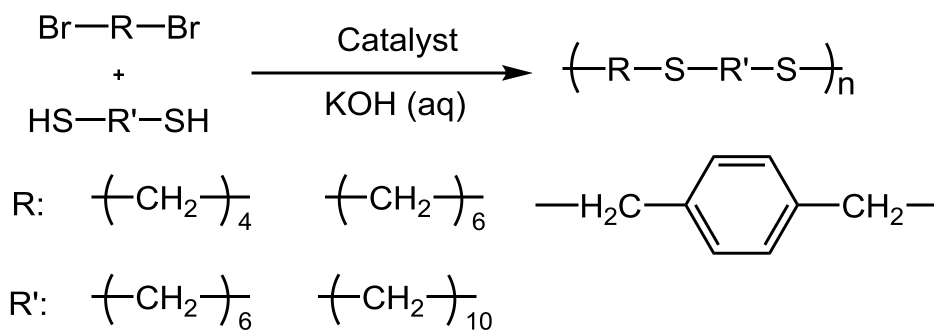



***3. The radical or ionic ring-opening reaction***

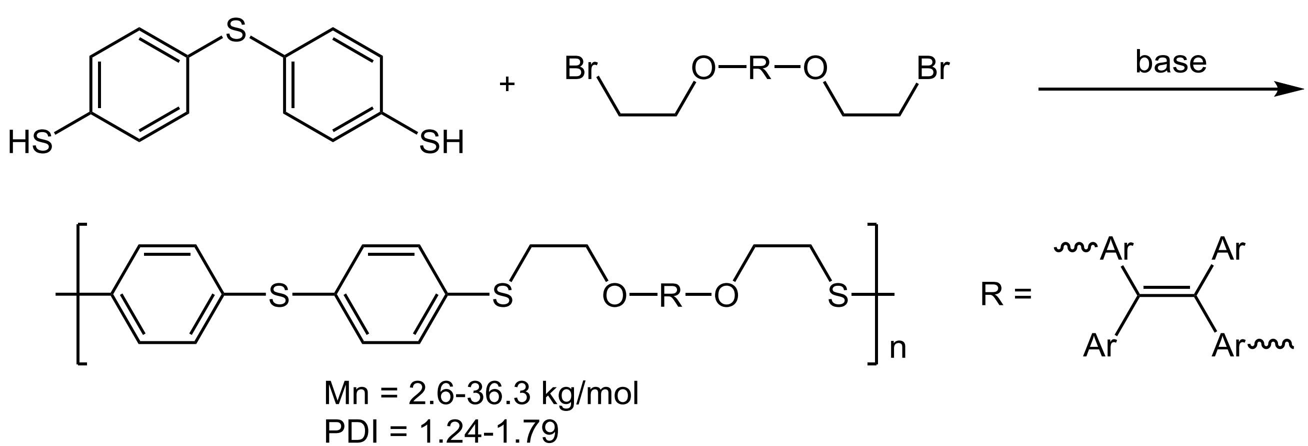


# Introduction

*The nucleophilic substitution reaction*



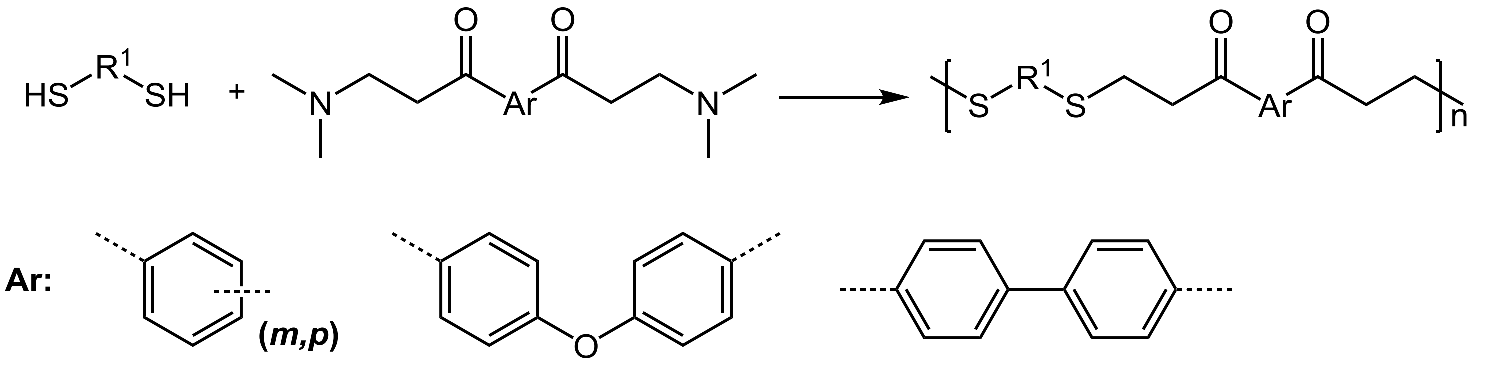

Ueda, M. et al. *J. Polym. Sci. Part C: Polym. Lett.* **1979**, *17*, 579.



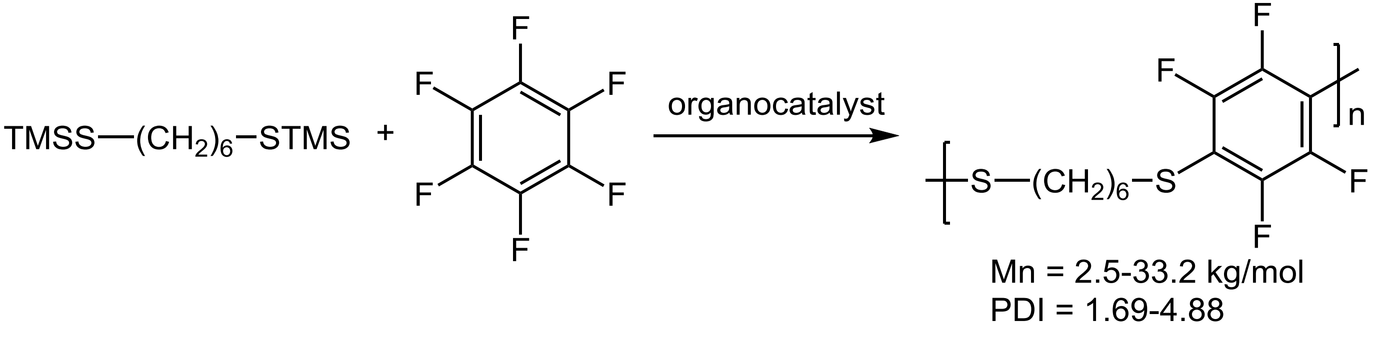

Tang, B. Z. et al. *Polym. Chem*. **2015**, *6*, 97.

# Introduction

*The nucleophilic substitution reaction*




Pilati, F. et al. *Polym. Commun.* **1983**, *24*, 156.

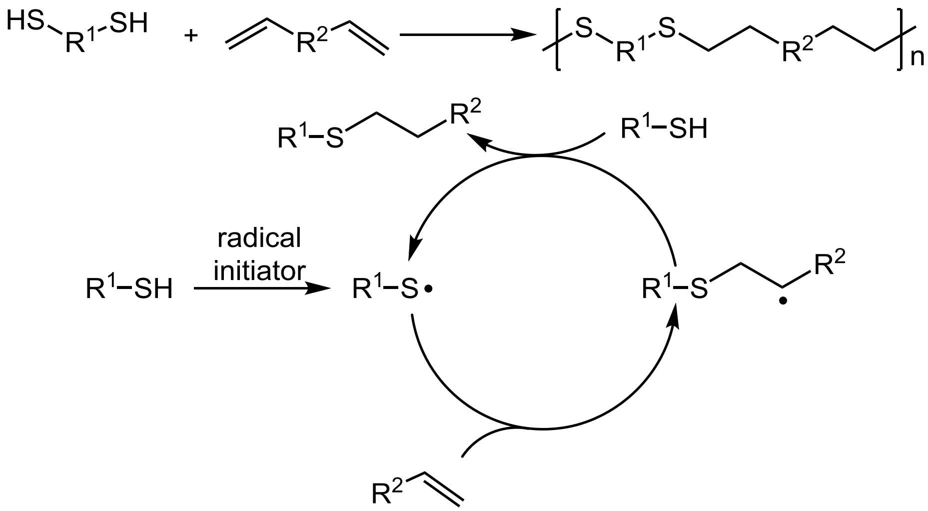



Hedrick, J. L. et al. *Nat. Commun.* **2017**, *8*, 166.

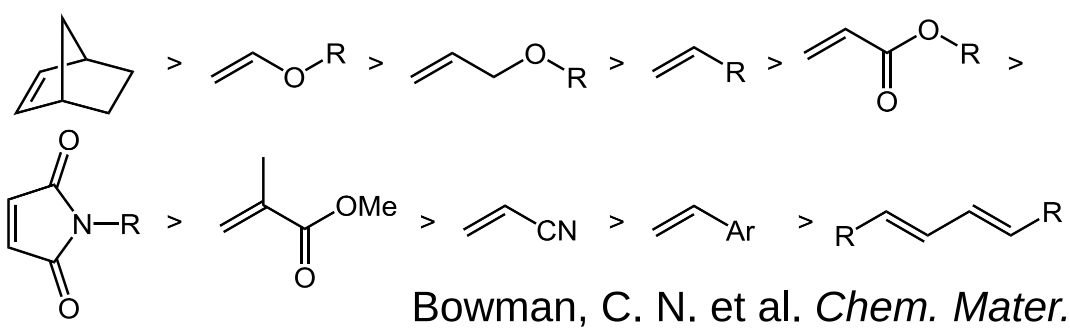
# Introduction

## *The thiol-ene/yne addition reaction*

- The free-radical thiol-ene addition




*Relative reactivity of some general ene-structures utilized in radical-initiated thiol-ene chemistry*

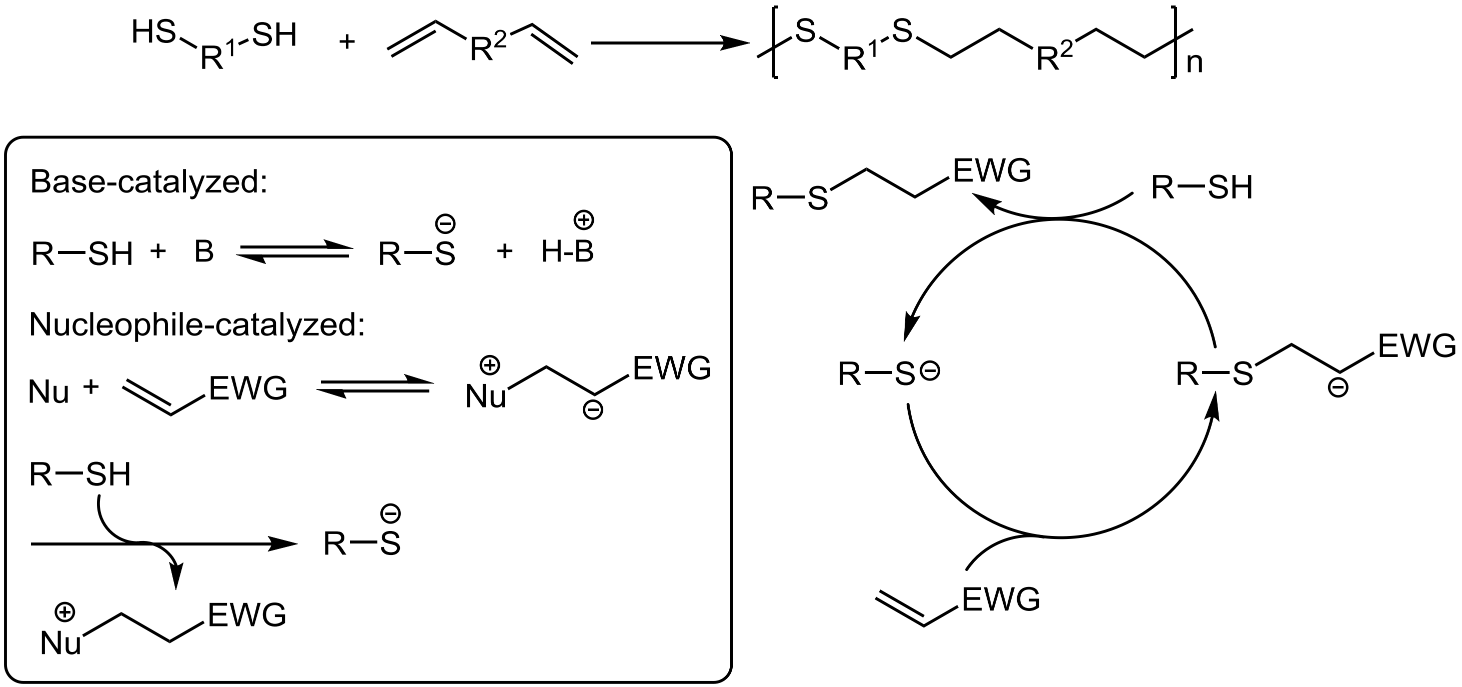


Bowman, C. N. et al. *Chem. Mater.* **2014**, *26*, 724.

# Introduction

*The thiol-ene/yne addition reaction*

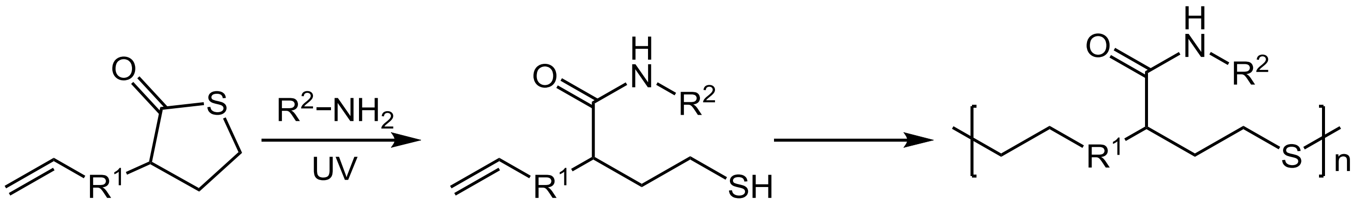
- The thiol-Michael addition (nucleophilic initiation or base catalysis)



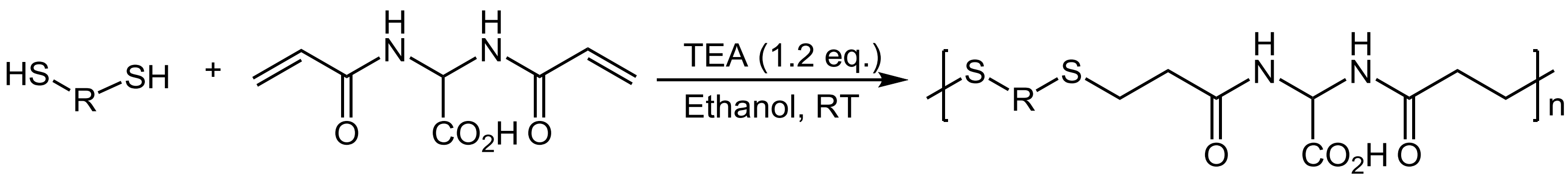

Bowman, C. N. et al. *Chem. Mater.* **2014**, *26*, 724.

# Introduction

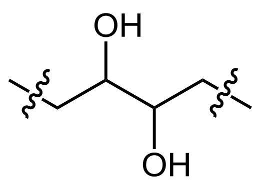
*The thiol-ene/yne addition reaction*




Du Prez, F. E. et al. *J. Am. Chem. Soc.* **2011**, *133*, 1678.
Metzger, J. O. et al. *Chem. Eur. J.* **2012**, *18*, 8201.




R = $(CH_2)_2$, $(CH_2)_3$, $(CH_2)_4$



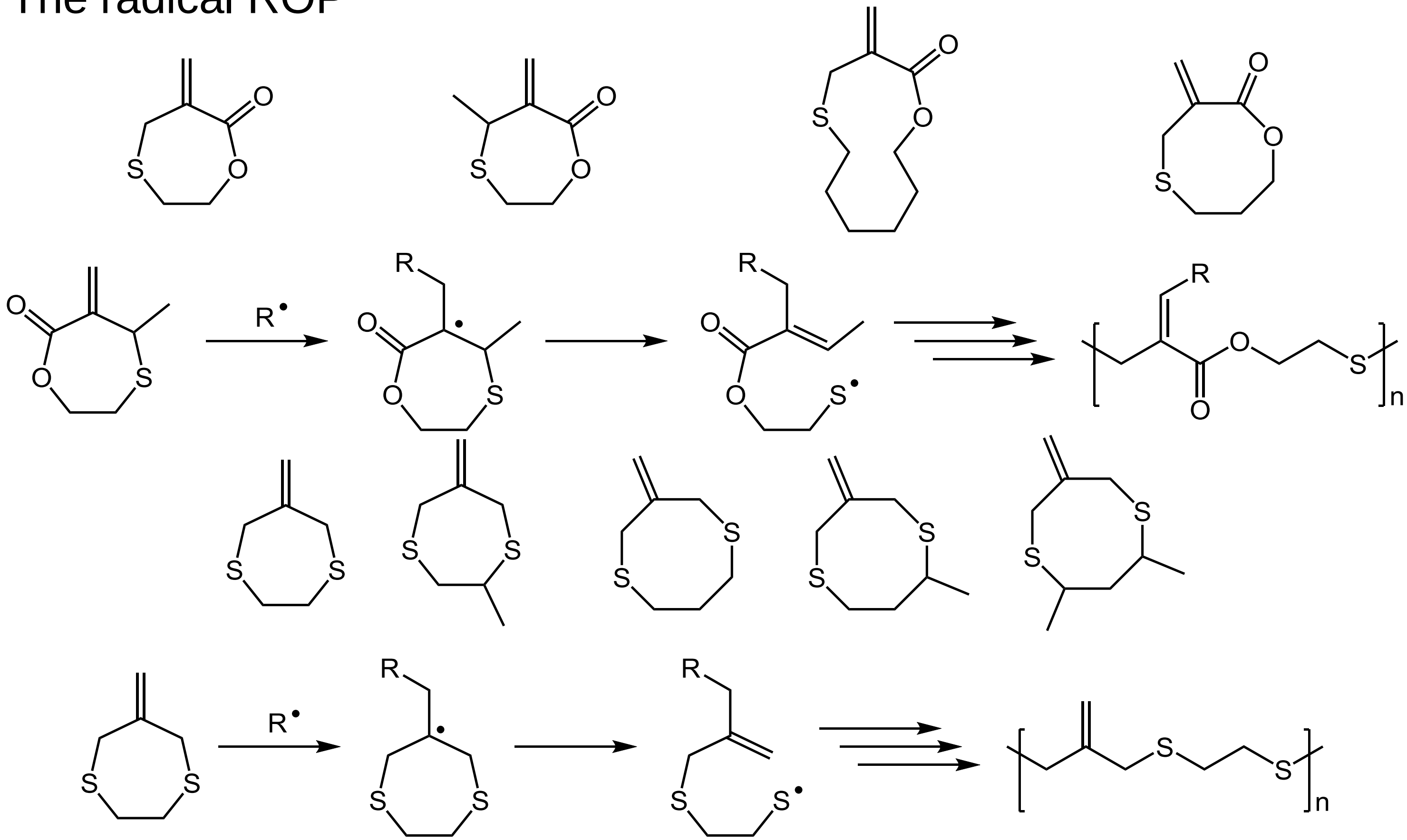

$M_n$ = 0.6-23.7 kg/mol
yield = 42-74%

Casolaro, M. et al. *Macromolecules* **1991**, *24*, 4554.

# Introduction

*Ring-Opening Polymerization*

- The radical ROP

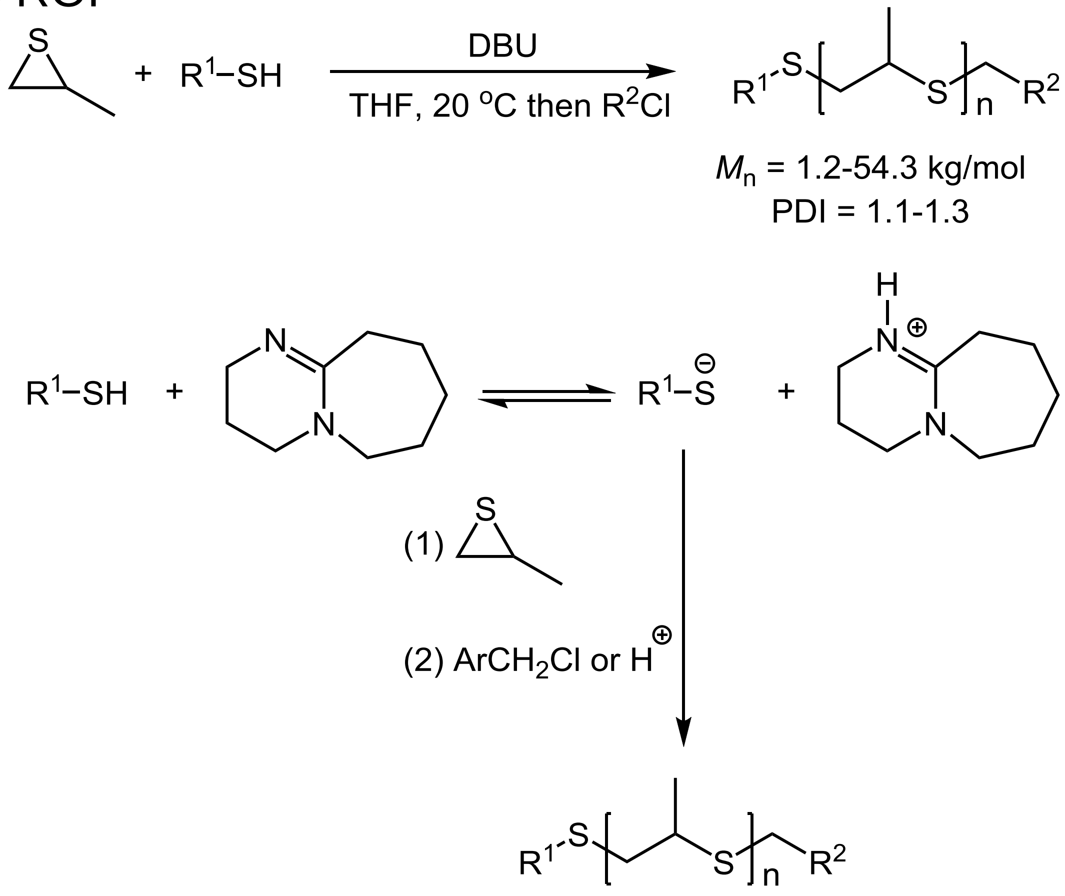



Thang, S. H. et al. *Macromolecules* **1994**, *27*, 7935.
Rizzardo, E. et al. *Macromolecules* **2001**, *34*, 3869.

# Introduction

*Ring-Opening Polymerization*

- The ionic ROP

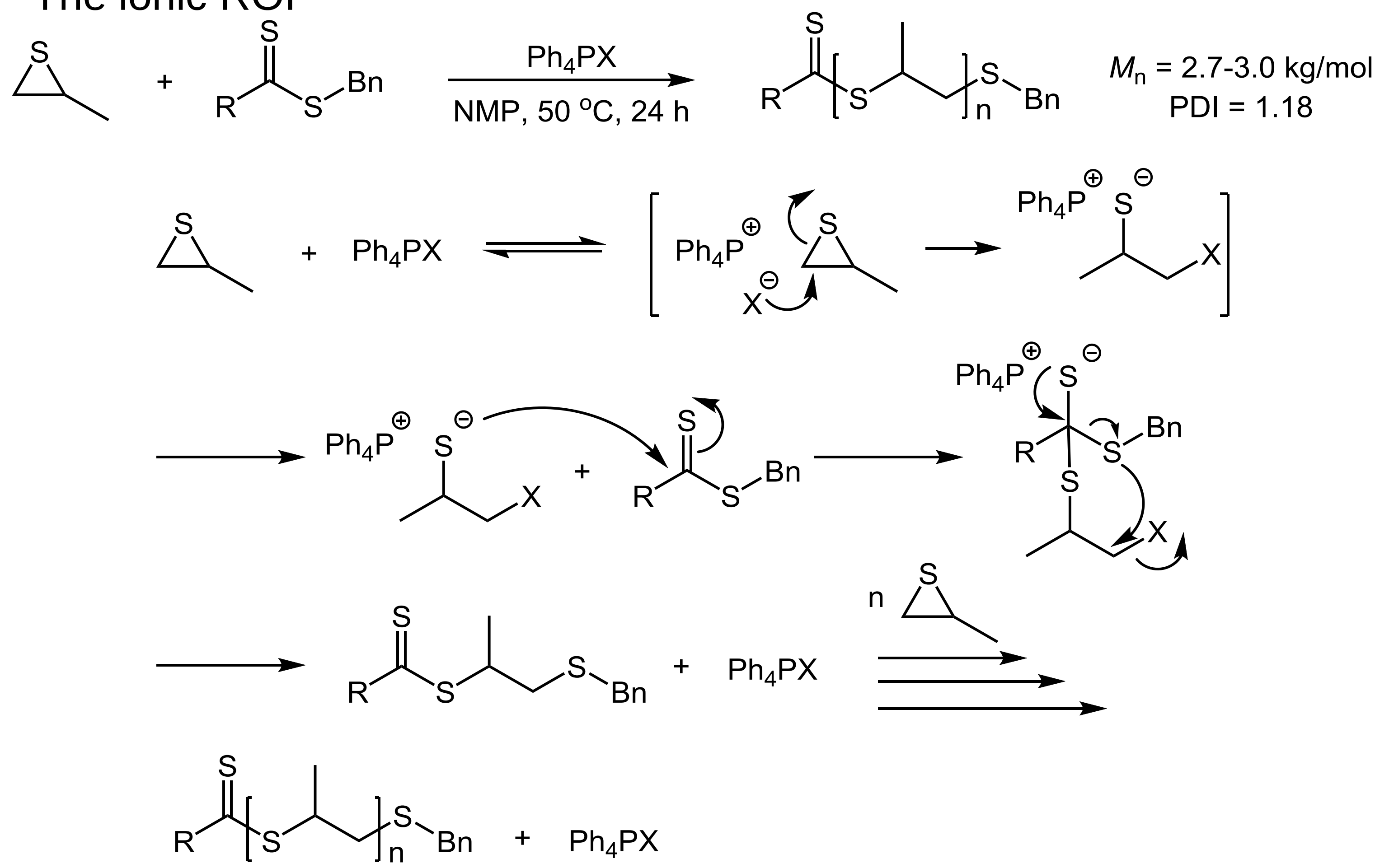



Levesque, G. et al. *Macromolecules* **1999**, *32*, 4485.

# Introduction

## *Ring-Opening Polymerization*

- The ionic ROP

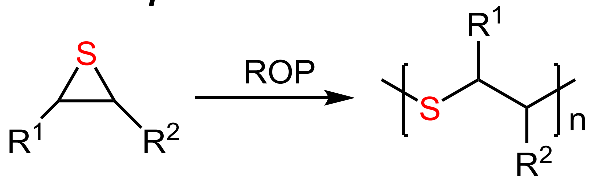



Nishikubo, T. et al. *Macromolecules* **2007**, *40*, 8129.

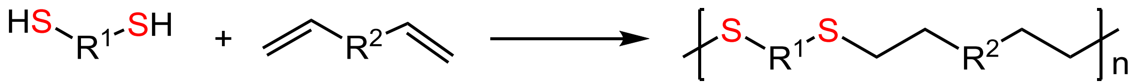
# Chemoselective Coupling of COS and Epoxides

## *Synthetic Methods to Poly(thioether)s*

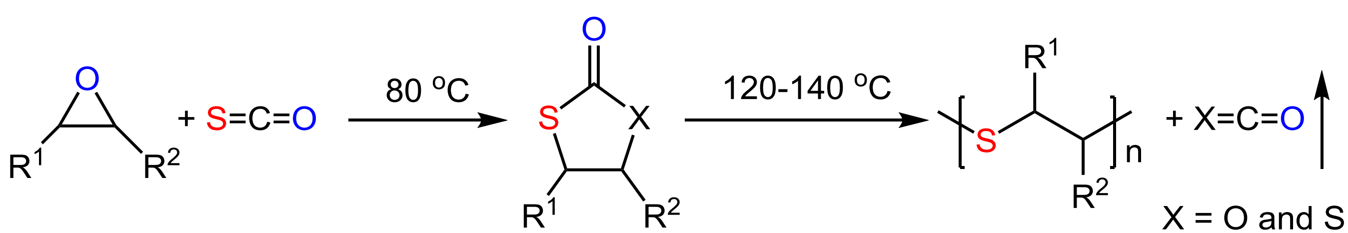
***1. ROP of episulfide***




***2. Thiol-ene polymerization***

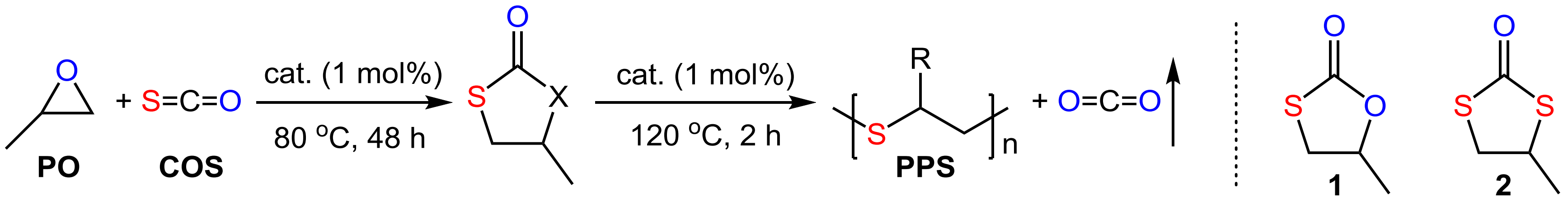



***3. This work: Closed-system one-pot two-steps***

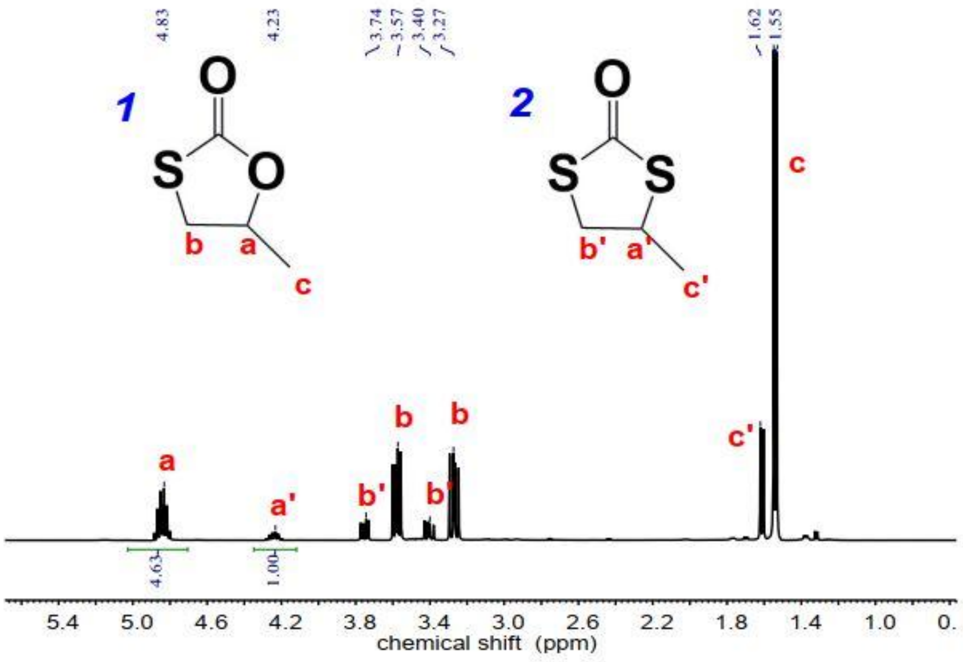



Zhang, X.-H. et al. *J. Am. Chem. Soc.* **2019**, *141*, 5490.

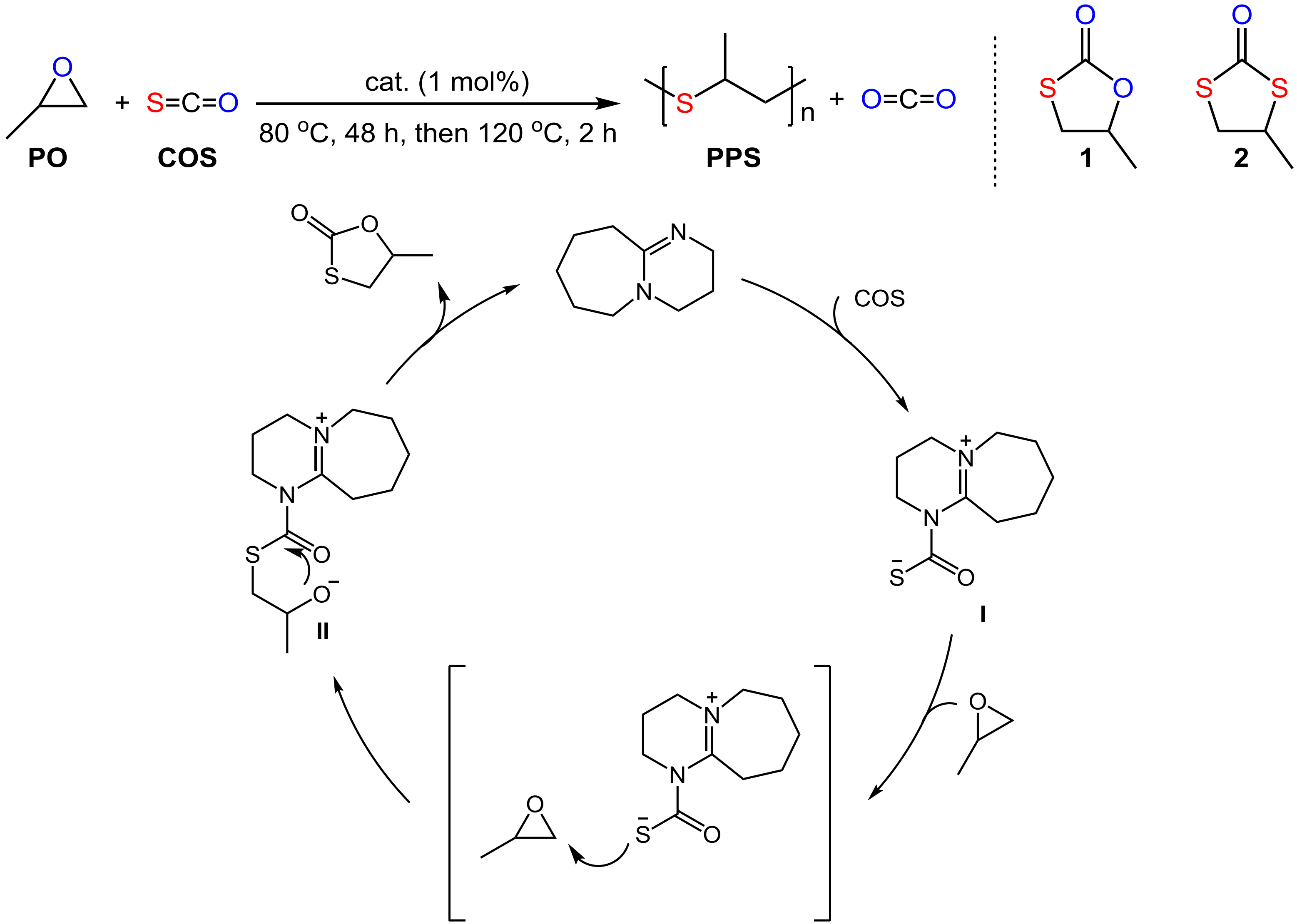
# Chemoselective Coupling of COS and Epoxides



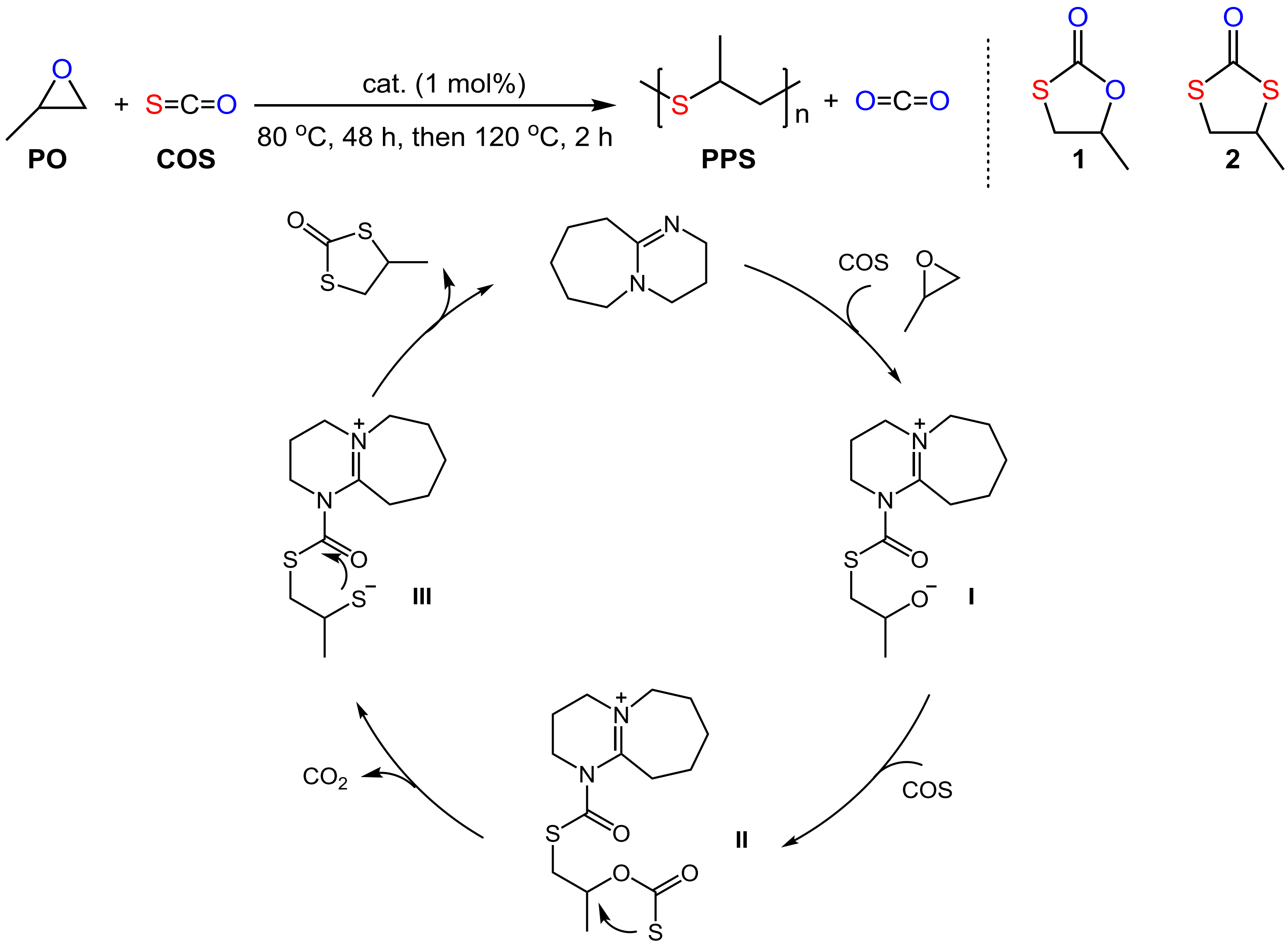

Mn = 14800 g/mol
PDI = 1.5
Yield = 99%



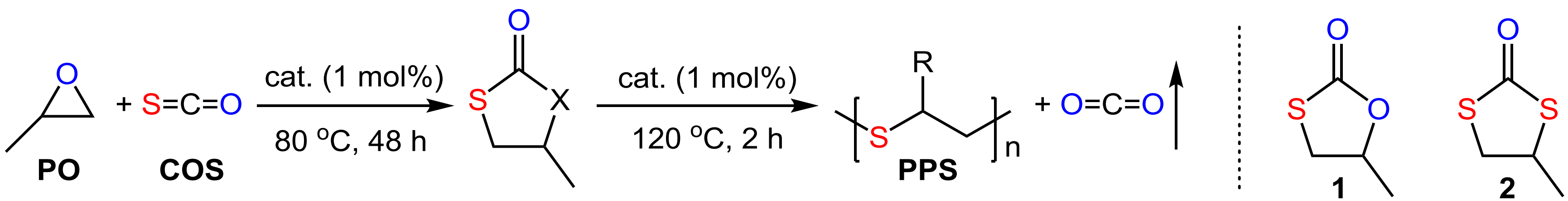
# Chemoselective Coupling of COS and Epoxides



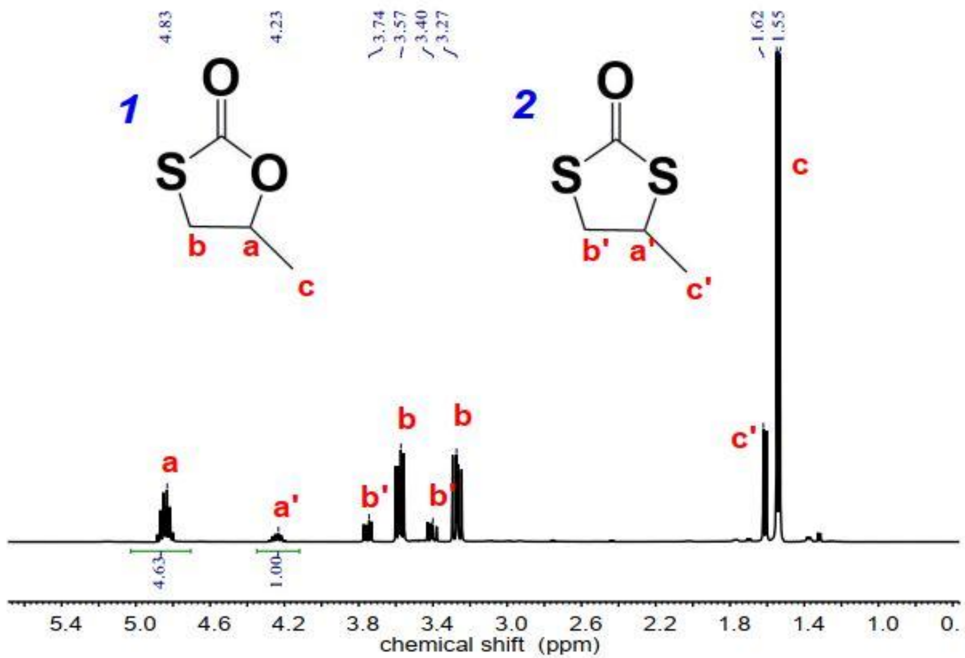
# Chemoselective Coupling of COS and Epoxides



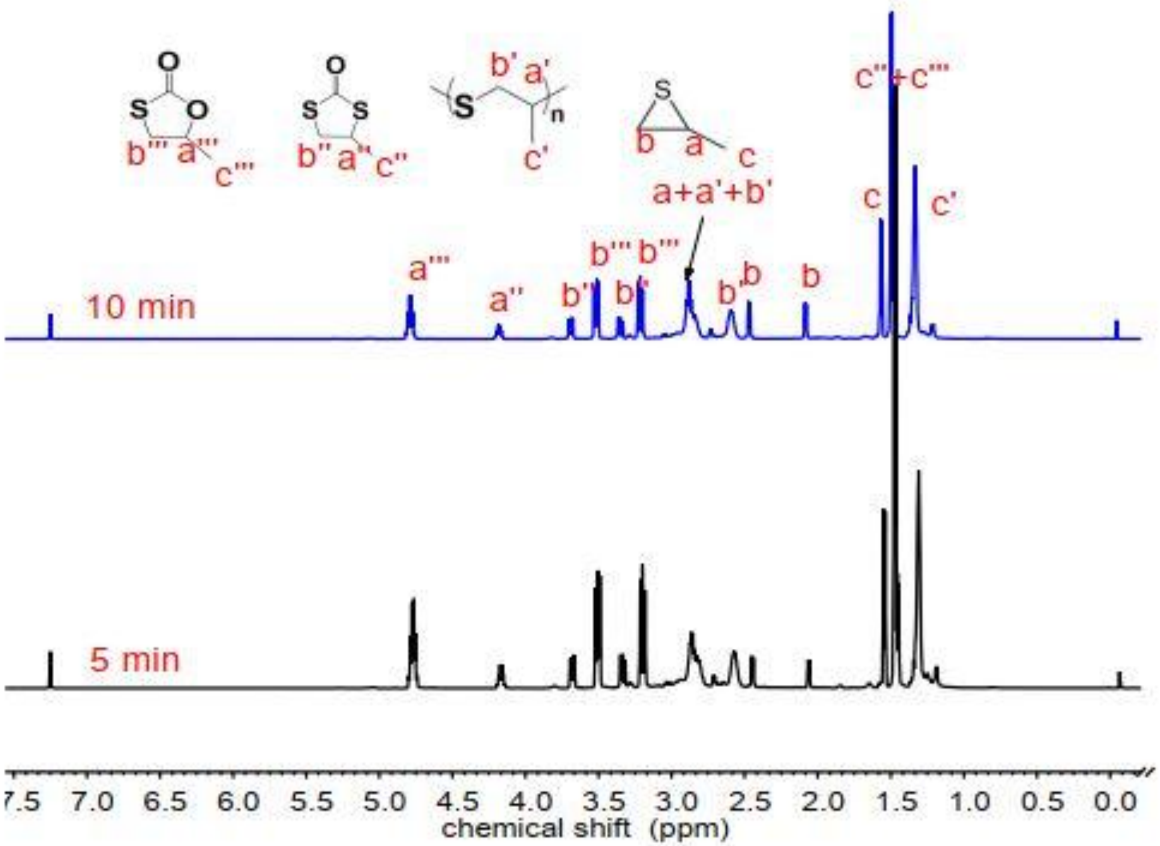
# Chemoselective Coupling of COS and Epoxides




Mn = 14800 g/mol
PDI = 1.5
Yield = 99%

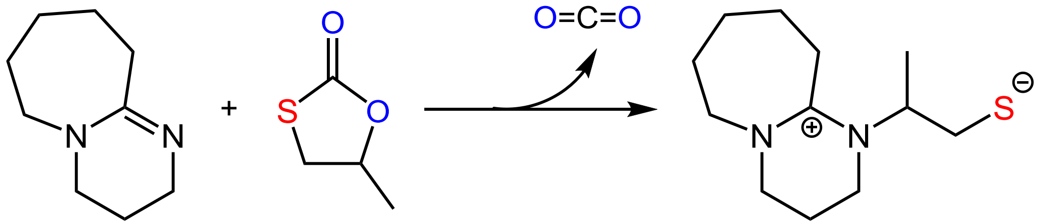


# Chemoselective Coupling of COS and Epoxides

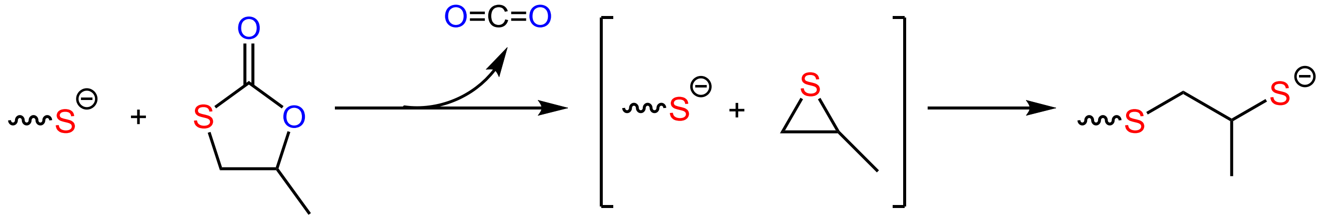


# Chemoselective Coupling of COS and Epoxides

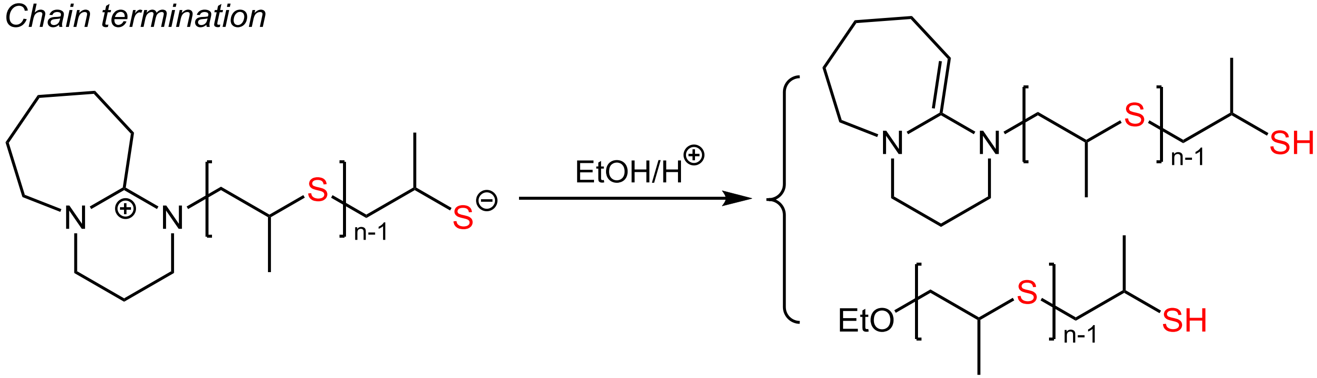
*(1) Chain initiation*



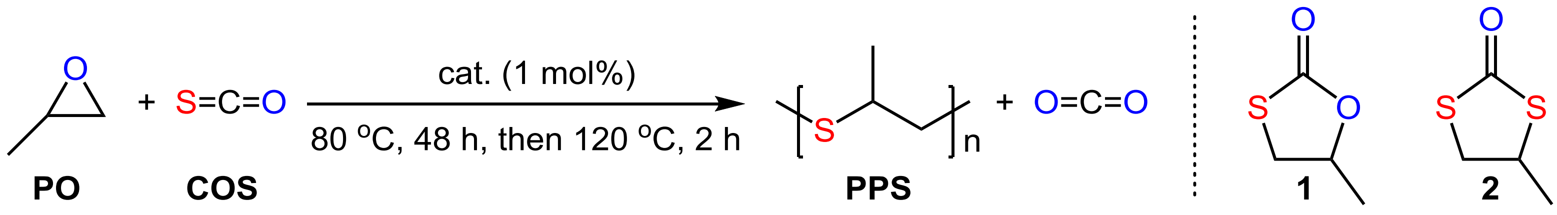

*(2) Chain growth*




*(3) Chain termination*



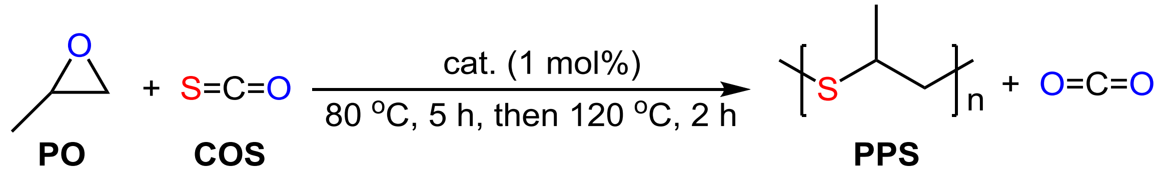
# Chemoselective Coupling of COS and Epoxides




| Entry [a] | COS/PO/DBU/TU | Yield (%) | $M_n$ (g/mol) [b] | Đ [b] |
|---|---|---|---|---|
| 1 [c] | 120/100/1/0 | 99 | 14800 | 1.5 |
| 2 [d] | 120/100/1/0 | 99 | 14400 | 1.5 |
| 3 [d] | 200/100/1/0 | 23 | 6000 | 1.6 |
| 4 [d,e] | 300/100/1/0 | 0 | 0 | 0 |
| 5 [f] | 120/100/1/2 | 99 | 16200 | 1.5 |

[a] Reactions were run in neat epoxide (1 mL) in a 10 mL autoclave. [b] Determined by GPC in THF. [c] Reactions were run at 80 °C for 48 h, releasing residual COS and running at 120 °C for 2 h. [d] Reactions were run at 80 °C for 48 h, and run at 120 °C for 2 h. [e] Only **1** and **2** were observed. [f] Reactions were run at 80 °C for 5 h, and run at 120 °C for 2 h.

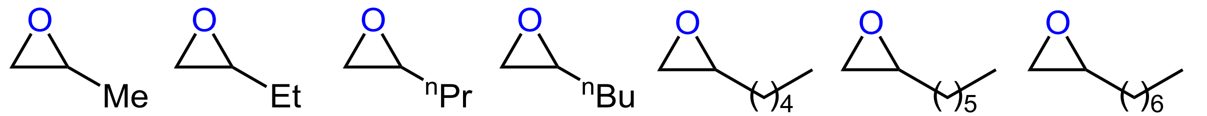
# Chemoselective Coupling of COS and Epoxides




| Entry [a] | Base | $M_n$ (g/mol) [b] | Đ [b] |
|---|---|---|---|
| 1 | DBU | 16200 | 1.5 |
| 2 | TBD | 10400 | 1.5 |
| 3 | DBN | 9900 | 1.5 |
| 4 | MTBD | 14500 | 1.6 |
| 5 | DMAP | 12500 | 1.5 |
| 6 | PPNCl | 15500 | 1.5 |

[a] Reactions were run with two steps at 80 °C for 5 h and were subsequently run at 120 °C for 2 h in neat epoxide (1 mL), COS:PO:Base:TU = 120:100:1:2. Yields of all entries were 99%. [b] Determined by GPC in THF.

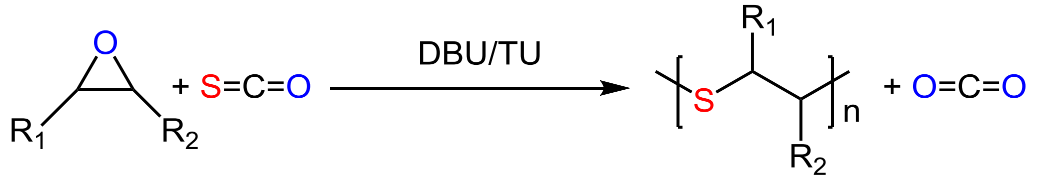
# Chemoselective Coupling of COS and Epoxides

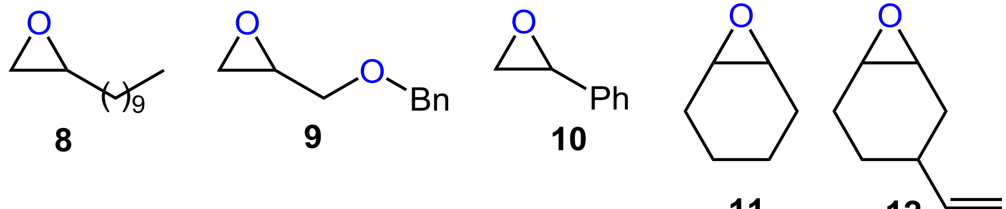




| Entry [a] | Epoxide | Yield (%) | $M_n$ (g/mol) [b] | Đ [b] | $T_g$ (°C) | $T_d$ (°C) |
|---|---|---|---|---|---|---|
| 1 | **1** | 99 | 16200 | 1.5 | -38.3 | 240 |
| 2 | **2** | 99 | 10700 | 1.5 | -45.7 | 235 |
| 3 | **3** | 99 | 9800 | 1.5 | -46.9 | 238 |
| 4 | **4** | 99 | 17300 | 1.6 | -49.9 | 257 |
| 5 | **5** | 99 | 12400 | 1.5 | -52.0 | 248 |
| 6 | **6** | 99 | 13500 | 1.5 | -56.3 | 251 |
| 7 | **7** | 99 | 12300 | 1.5 | -58.4 | 253 |

[a] Reactions were run with two steps, run at 80 °C for 5 h and subsequently run at 120 °C for 5 h in neat epoxide (1 mL), COS:PO:Base:TU = 120:100:1:2. Yields of all entries were 99%. [b] Determined by GPC in THF.

# Chemoselective Coupling of COS and Epoxides



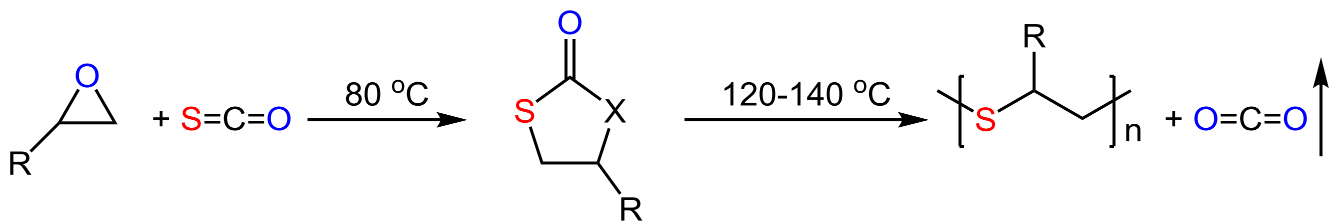

8 9 10 11 12

| Entry [a] | Epoxide | Yield (%) | $M_n$ (g/mol) [b] | Đ [b] | $T_g$ (ºC) | $T_d$ (ºC) |
|---|---|---|---|---|---|---|
| 1 | **8** | 99 | 10800 | 1.6 | -45.8 | 254 |
| 2 | **9** | 99 | 16400 | 1.6 | -14.2 | 255 |
| 3 [c] | **10** | 90 | 2300 | 1.5 | 23.9 | 227 |
| 4 [c] | **11** | 91 | 2100 | 1.4 | 53.4 | 224 |
| 5 [c] | **12** | 92 | 3400 | 1.4 | 48.7 | 217 |

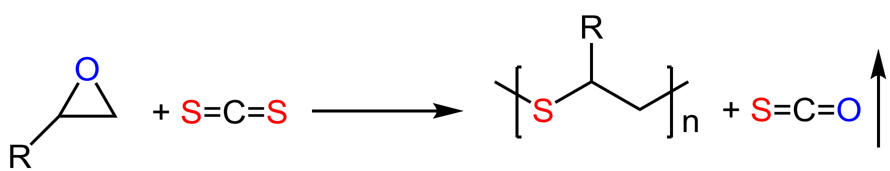
[a] Reactions were run with two steps, run at 80 ºC for 5 h and subsequently run at 120 ºC for 5 h in neat epoxide (1 mL), COS:PO:Base:TU = 120:100:1:2. [b] Determined by GPC in THF. [c] 80 ºC/ 5 h and 140 ºC/ 5 h for two steps.

# Chemoselective Coupling of $CS_2$ and Epoxides

***1. Previous work: Closed-system one-pot two-steps***



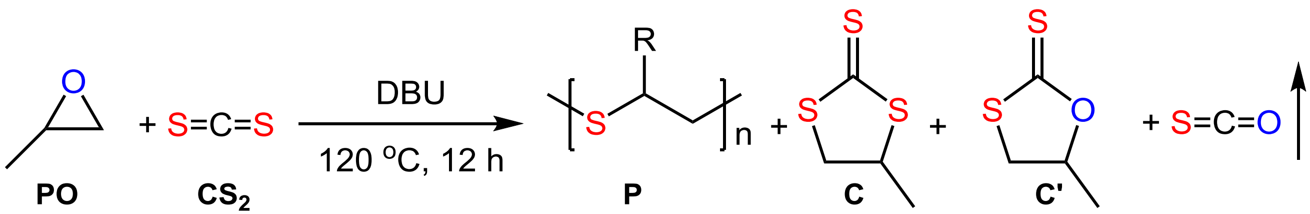

***2. This work:***




***Exchange of Oxygen and Sulfur Atoms***

Zhang, X.-H. et al. *Macromolecules* **2020**, *53*, 233.

# Chemoselective Coupling of $CS_2$ and Epoxides

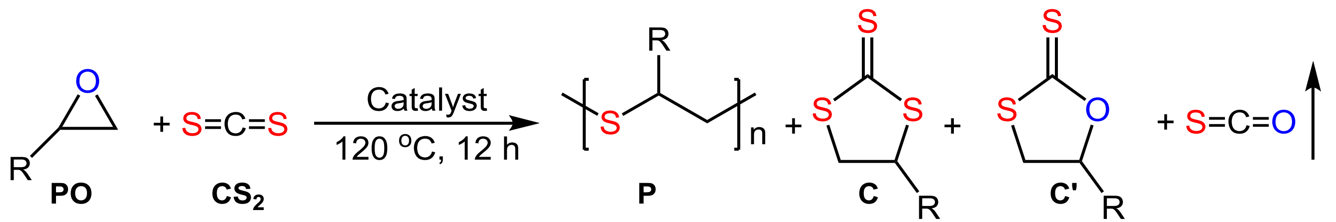


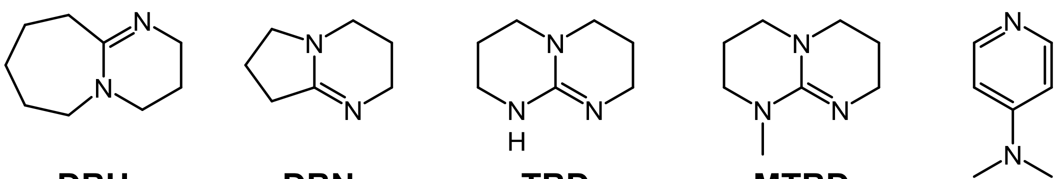

| Entry [a] | Solvent | Tem. (°C) | P:C:C' | Yield (%) | $M_n$ (g/mol) [b] | Đ [b] |
|---|---|---|---|---|---|---|
| 1 | TOL | 120 | 78:22:0 | 70 | 1800 | 1.5 |
| 2 | TOL | 100 | 0:43:57 | 0 | - | - |
| 3 | TOL | 140 | 50:50:0 | 40 | 1100 | 1.5 |
| 4 | DMF | 120 | 0:0:0 | 0 | - | - |
| 5 | $C_6H_3Cl_3$ | 120 | 30:70:0 | 21 | 1200 | 1.5 |

[a] Reactions were run at 120 °C for 12 h in solvent (5 mL), $CS_2$:PO:Cat. = 150:100:1. [b] Determined by GPC in THF.

The use of less polar solvent benefits the production of PPS.

# Chemoselective Coupling of $CS_2$ and Epoxides



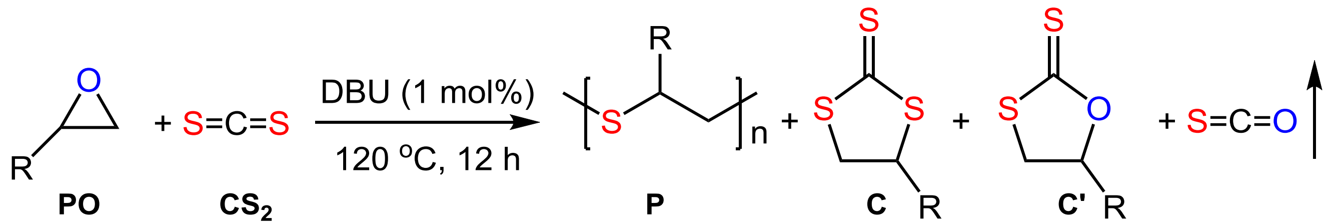
**DBU** **DBN** **TBD** **MTBD** **DMAP**

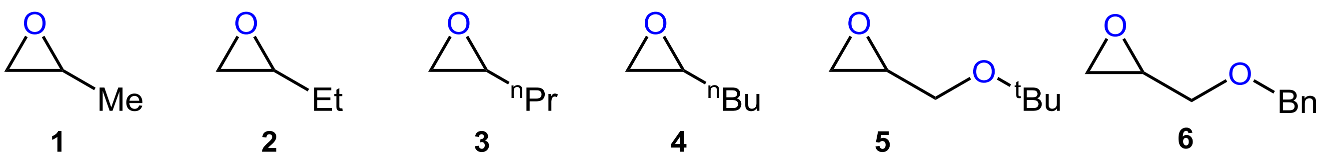
| Entry [a] | Base | P:C:C’ | Yield (%) | $M_n$ (g/mol) [b] | Đ [b] |
|---|---|---|---|---|---|
| 1 | DBU | 80:20:0 | 73 | 1800 | 1.5 |
| 2 | TBD | 91:9:0 | 83 | 1900 | 1.5 |
| 3 | DBN | 74:26:0 | 61 | 1400 | 1.4 |
| 4 | MTBD | 83:17:0 | 69 | 1700 | 1.5 |
| 5 | DMAP | 0:43:57 | 0 | - | - |

[a] Reactions were run at 120 °C for 12 h in toluene (5 mL), $CS_2$:PO:Cat. = 150:100:1. [b] Determined by GPC in THF.

The organic base with high basicity benefits the production of PPS.

# Chemoselective Coupling of $CS_2$ and Epoxides

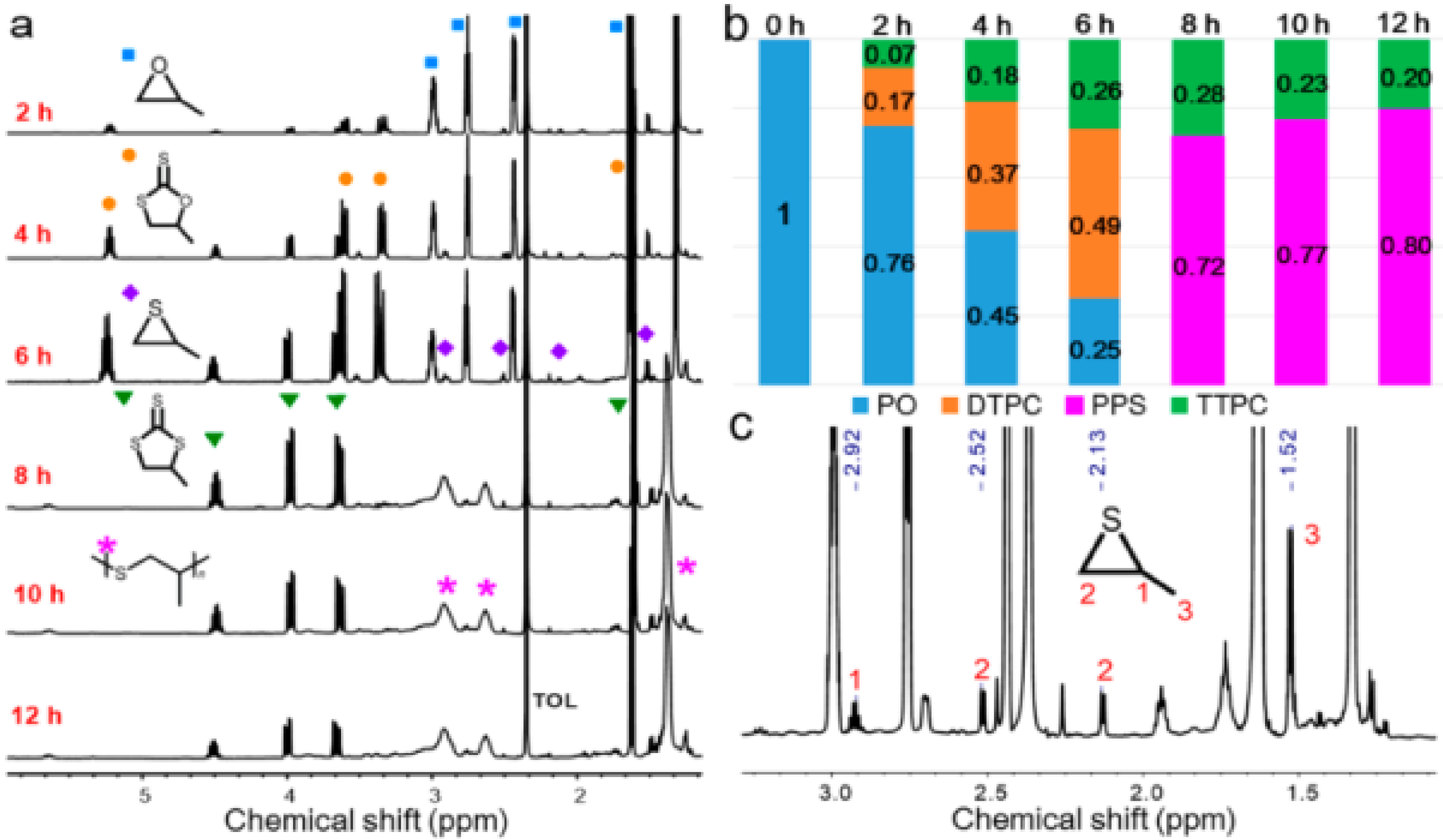


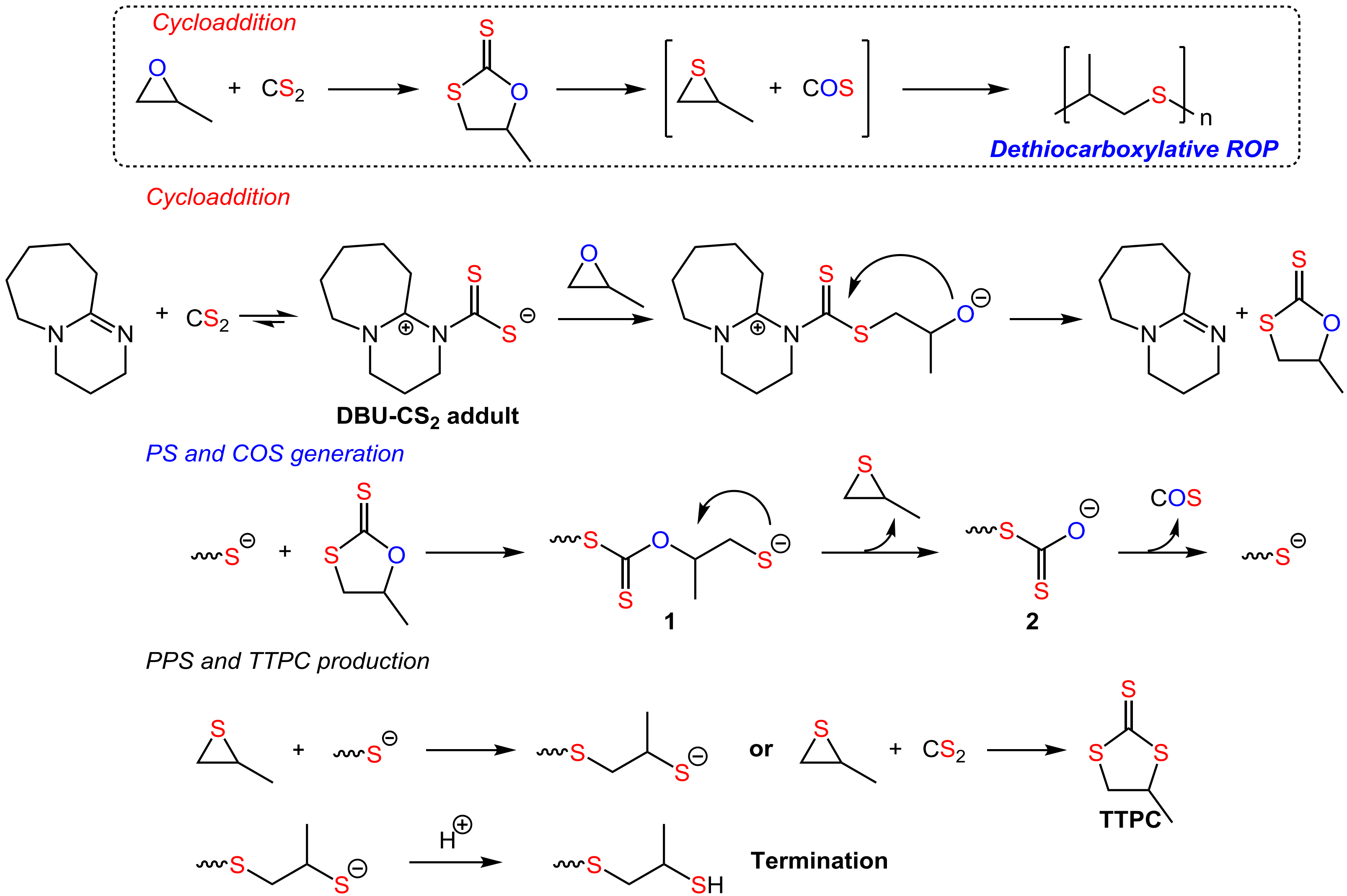

| Entry [a] | Epoxide | P:C:C' | Yield (%) | $M_n$ (g/mol) [b] | Đ [b] |
|---|---|---|---|---|---|
| 1 | **1** | 80:20:0 | 73 | 1800 | 1.5 |
| 2 | **2** | 54:46:0 | 41 | 2300 | 1.4 |
| 3 | **3** | 91:9:0 | 80 | 3100 | 1.5 |
| 4 | **4** | 76:24:0 | 59 | 5100 | 1.2 |
| 5 | **5** | 70:30:0 | 47 | 4400 | 1.4 |
| 6 | **6** | 60:40:0 | 44 | 4100 | 1.3 |

[a] Reactions were run at 120 °C for 12 h in toluene (5 mL), $CS_2$:PO:Cat. = 150:100:1. [b] Determined by GPC in THF.

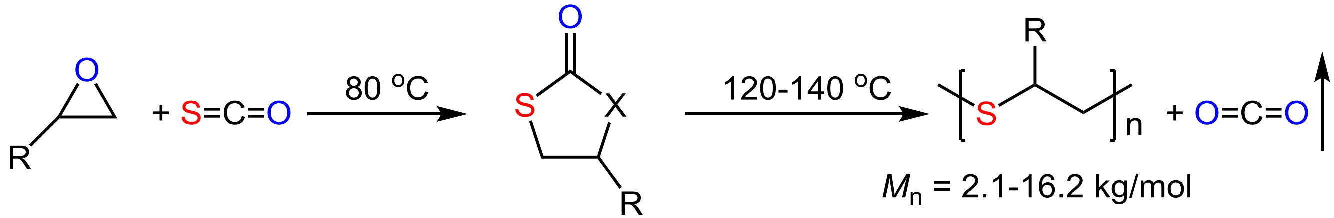
# Chemoselective Coupling of $CS_2$ and Epoxides



# Chemoselective Coupling of $CS_2$ and Epoxides



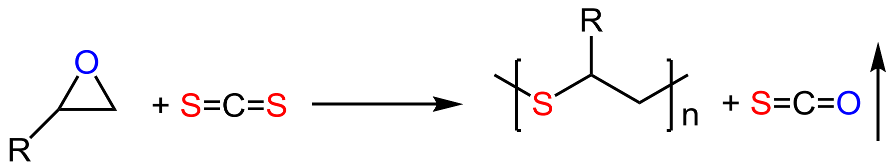
# Summary




$M_n$ = 2.1-16.2 kg/mol
PDI = 1.4-1.6
yield = 90-99%

Zhang, X.-H. et al. *J. Am. Chem. Soc.* **2019**, *141*, 5490.

***Exchange of Oxygen and Sulfur Atoms***




$M_n$ = 1.8-5.1 kg/mol
PDI = 1.2-1.5
yield = 41-80%

Zhang, X.-H. et al. *Macromolecules* **2020**, *53*, 233.

# Writing Strategy

含硫聚合物的重要性

↓

聚硫醚的应用及其有限的合成方法

↓

发展新方法合成聚硫醚

# The First Paragraph

Sulfur has caused widespread interests in modern polymers and materials science. The interposition of sulfur into polymeric materials can endow superior properties, e.g., enhanced electrical, optical, mechanical, and thermal features, thereby rendering these polymers with promising applications in rechargeable batteries, biological and optical materials, and so on. Poly(thioether)s, as a kind of highly desired sulfur- rich polymer, are very promising in applications of energy materials and functional biomaterials. However, the current synthetic methods to poly(thioether)s are limited to the ring-opening polymerization (ROP) of episulfide and the dithiol−diene click polymerization, which greatly limit their wide applications due to uncommon monomers. The development of robust and versatile methods to access sulfur-containing polymers from readily available monomers is highly desired.

# Writing Strategy

总结本文具体工作

↓

概况本文工作亮点

↓

提出之后的研究方向

# The Last Paragraph

We disclosed a chemoselective coupling reaction of $CS_2$ with epoxides for producing poly(thioether)s and COS in one pot. This strategy utilized the O/S ERs, leading to the exchange of sulfur atom in $CS_2$ with oxygen atom in epoxide. The mechanistic study suggested the process underwent the cycloaddition of $CS_2$ to epoxide and the dethiocarboxylative ROP of the generated cyclic dithiocarbonates. Moreover, this reaction could be conducted in ambient air with organic base as a catalyst (initiator) and produced COS and various poly(thioether)s with up to 10 g in one batch. Therefore, this is a robust, metal-free, and efficient approach to poly(thioether)s that can be operated in the ambient air conditions. Our ongoing efforts are to seek efficient catalysts to better control the polymerization process, the detailed mechanism knowledge, and applications of the poly(thioether)s in materials science.

# Representative Examples

Remarkably, organic bases catalyzed the coupling reaction and initiated the ROP, thus **a method of killing two birds with one stone**. **(这个方法具有一石二鸟的优点)**.

Clearly, such ROP process was affected by the chemical equilibrium that **was closely related to** the pressure of the system. **(与……密切相关)**.

The interposition of sulfur into polymeric materials can **endow** superior properties, e.g., enhanced electrical, optical, mechanical, and thermal features, thereby rendering these polymers with promising applications in rechargeable batteries, biological and optical materials, and so on. (赋予).

# Acknowledgement

**Thanks for your attention**