Comparison of the reactivity of mercaptosilane and sulfur silane in a model study

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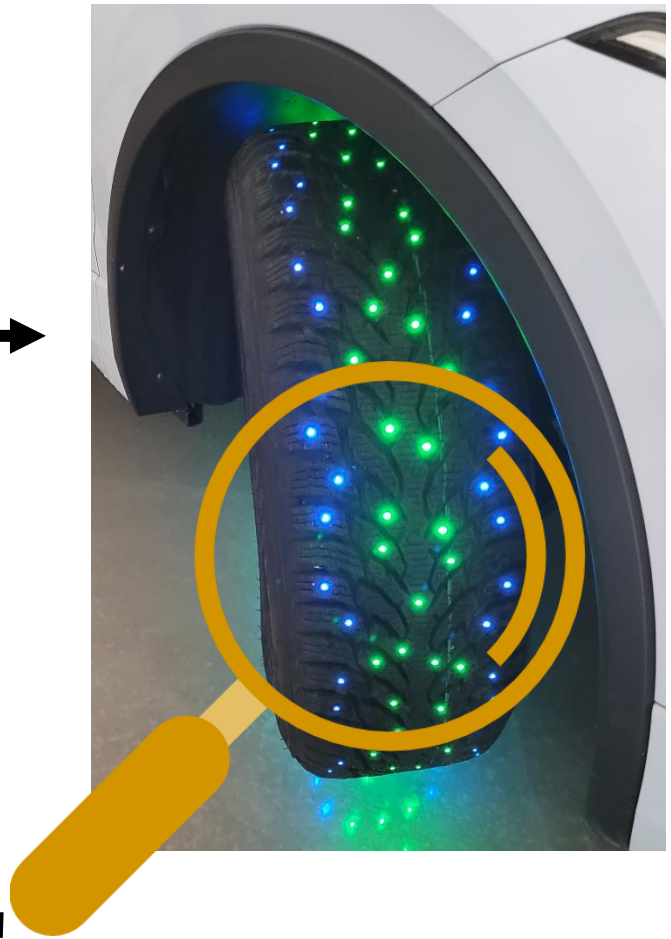
UNIVERSITY OF TWENTE.

Elastomer Technology and Engineering

Tires - adjusted to the needs for mobility

A long way to go!



Silica / silane inside!

(239) Experiment: WOODEN WHEELS on a real CAR – YouTube; https://electricliterature.com/7-books-about-magic-coming-back/

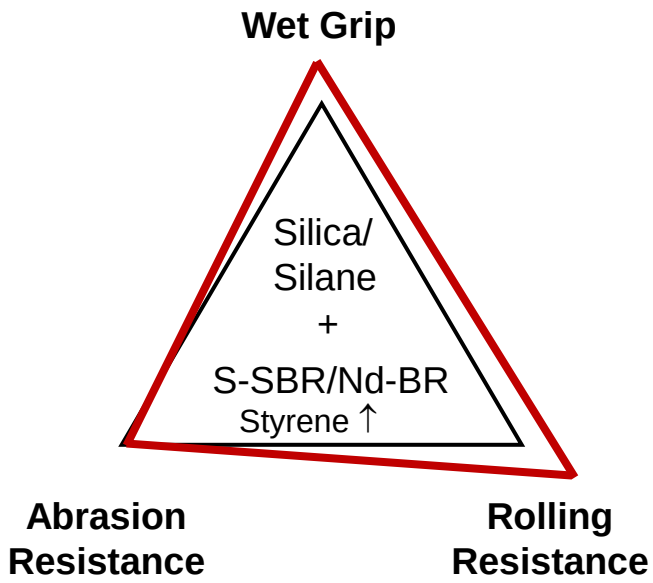
How to extend the magic triangle further?

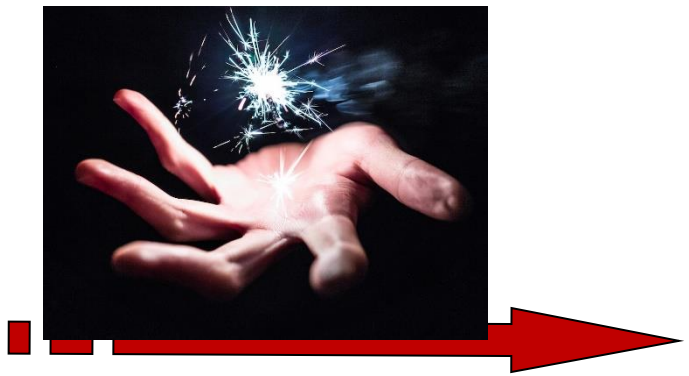
Improve the silica / silane technology further!

https://electricliterature.com/7-books-about-magic-coming-back/

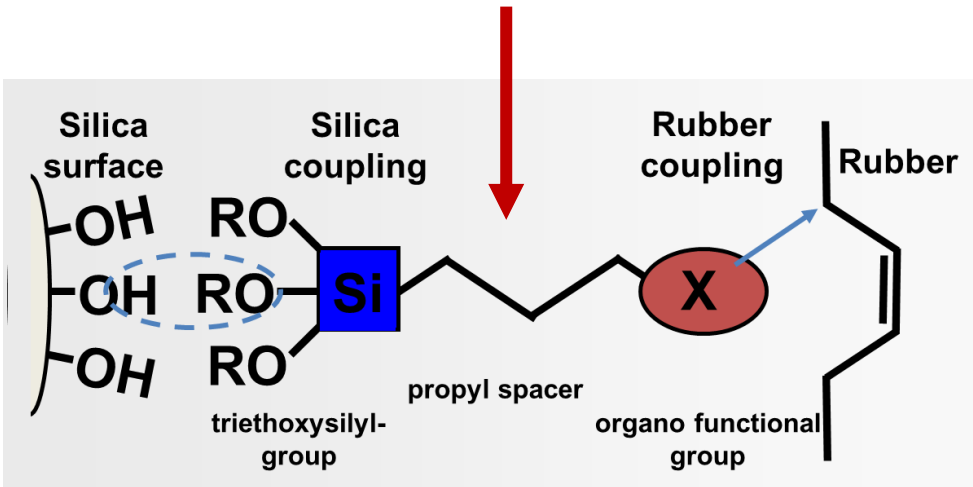
How to extend the magic triangle further?

Improve the silica / silane technology further!



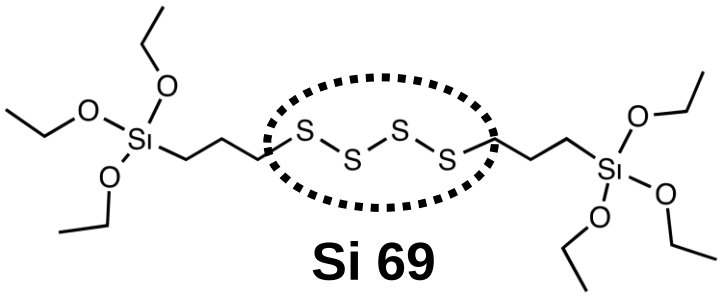


One possibility: Vary the type of silane



https://electricliterature.com/7-books-about-magic-coming-back/

Silica-filled tire tread compound: Mercaptosilane versus Sulfur Silane



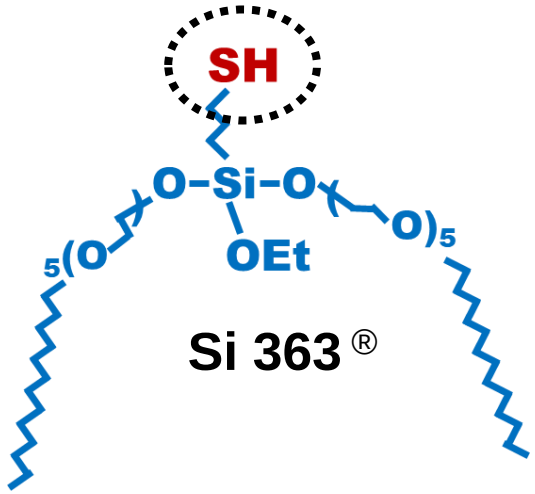
Si 69

Property Index	Si 69®	Si 363®
Mooney Viscosity	100	112
Scorch time	100	143
⊿G'(0.56%-100%)	100	50
tanδ at 60°C	100	75

*Lower value = better

worse processibility

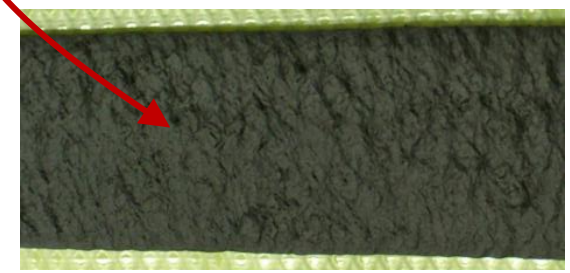
good dispersion



Si 363 ®

Si 69 ®

Si 363 ®



extruded product in lab. test →

Which mechanism is responsible for improved dispersion but worse processing?

Model study

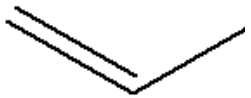
Does an early coupling towards double bonds in the polymer cause the processing issues of mercaptosilanes?

If so: Towards which double bond?

cis

trans

vinyl



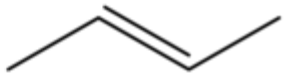
Model study:
Start with small molecules

cis

C3H

Cis-3-hexene

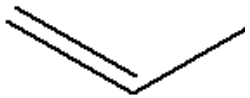
trans

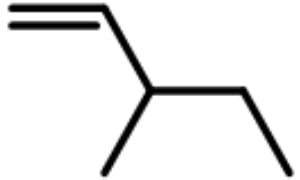


T3H

Trans-3-hexene

vinyl

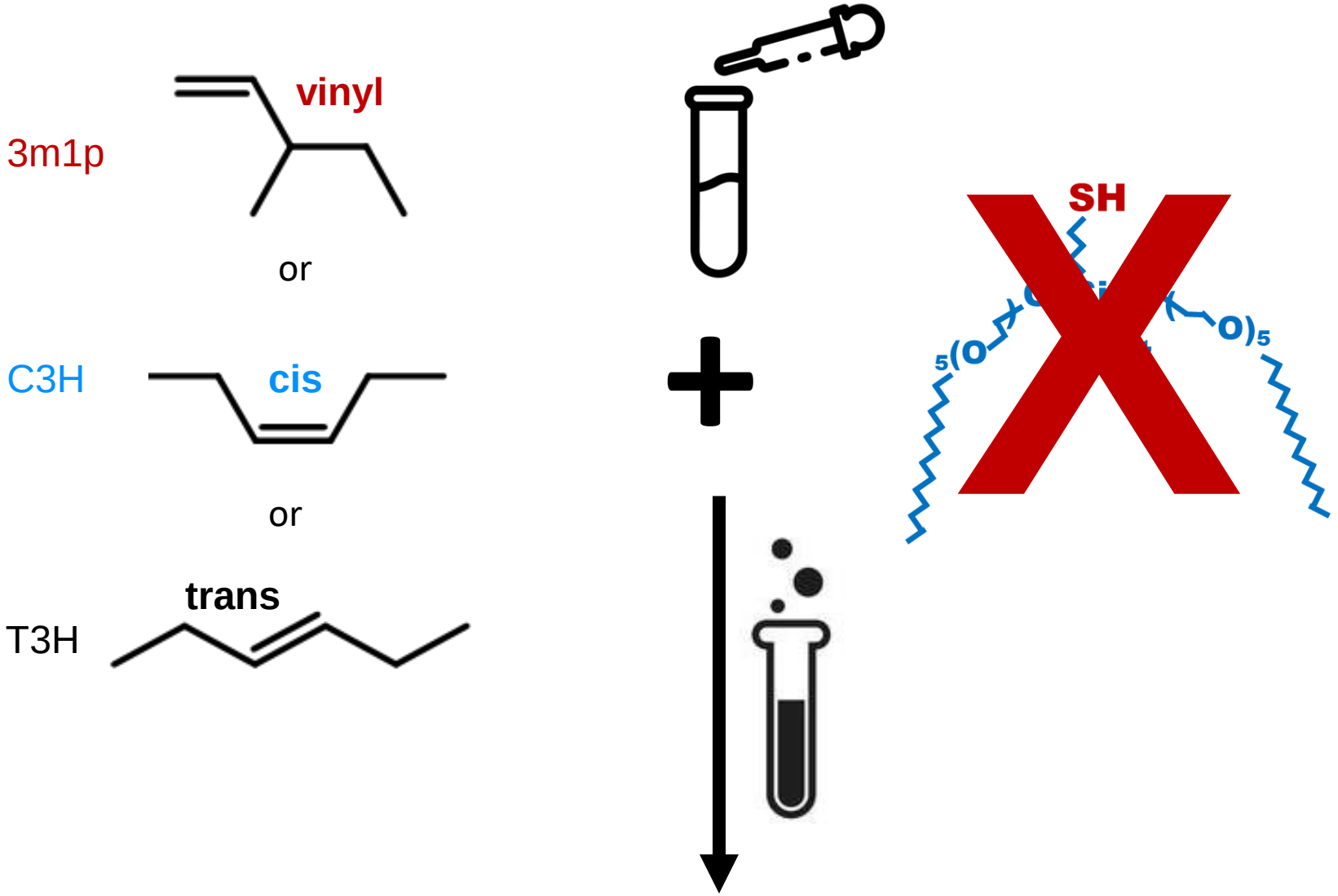




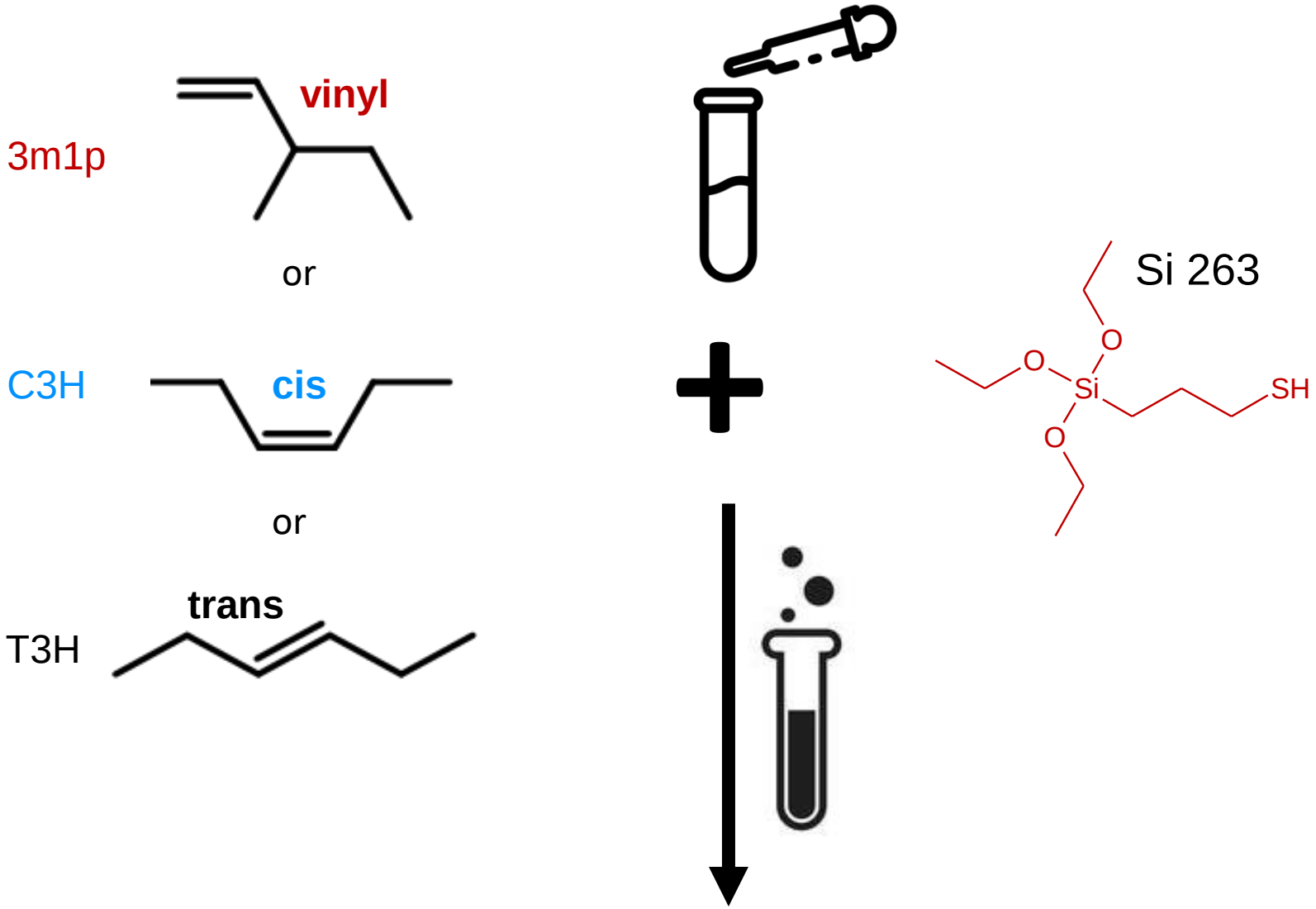
3m1p

3-methyl-1-pentene

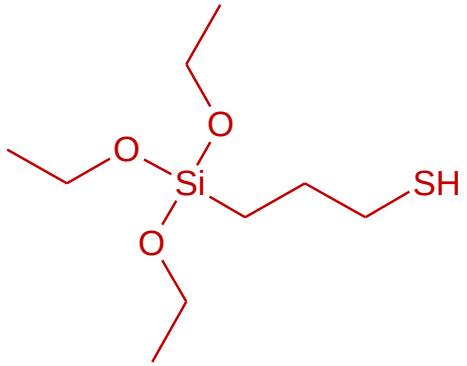
Model study with vinyl / cis olefin in decane



Model study with vinyl / cis olefin in decane



Model study with trans olefin in decane



+

170°C

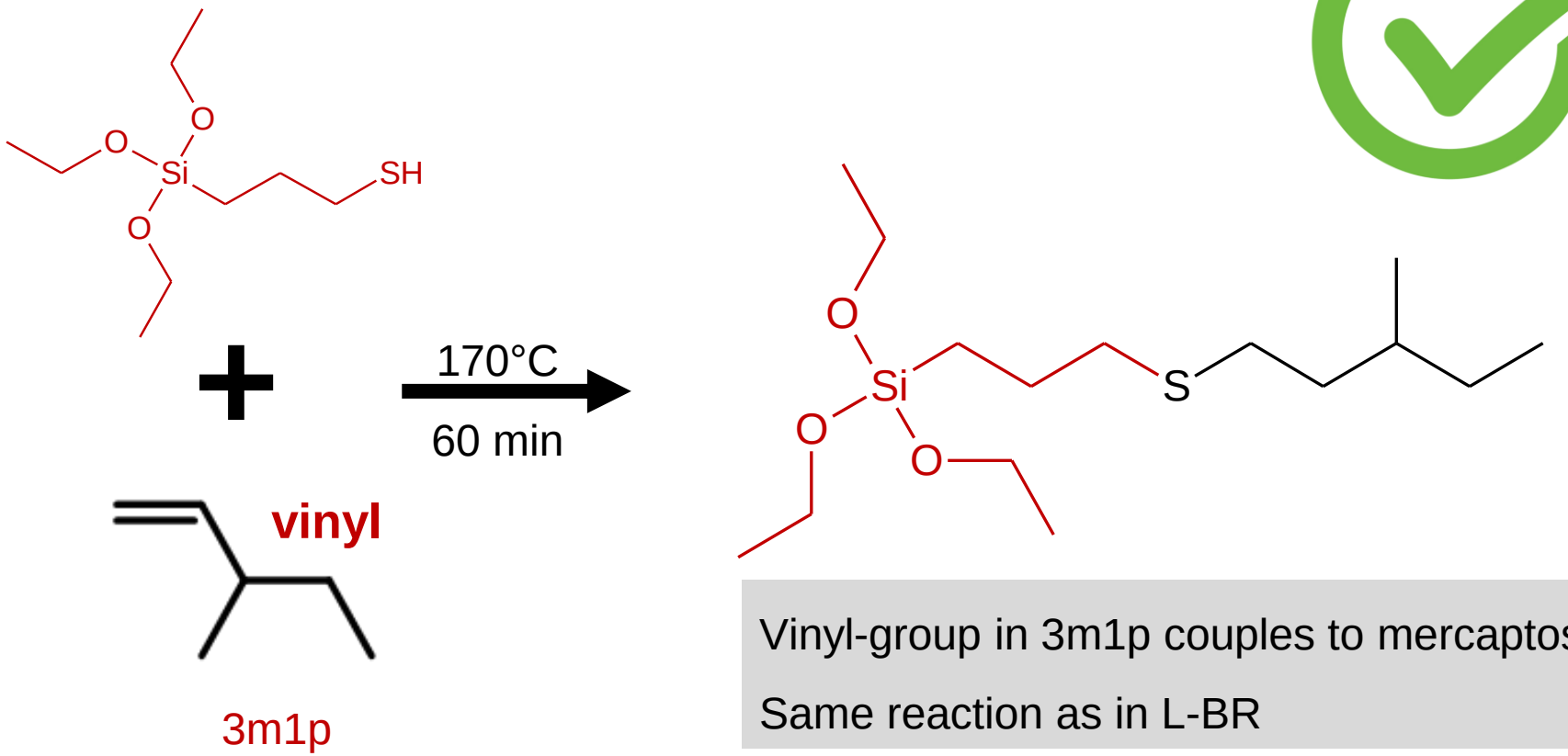
60 min

No reaction product.

trans

T3H

Model study with vinyl olefin in decane

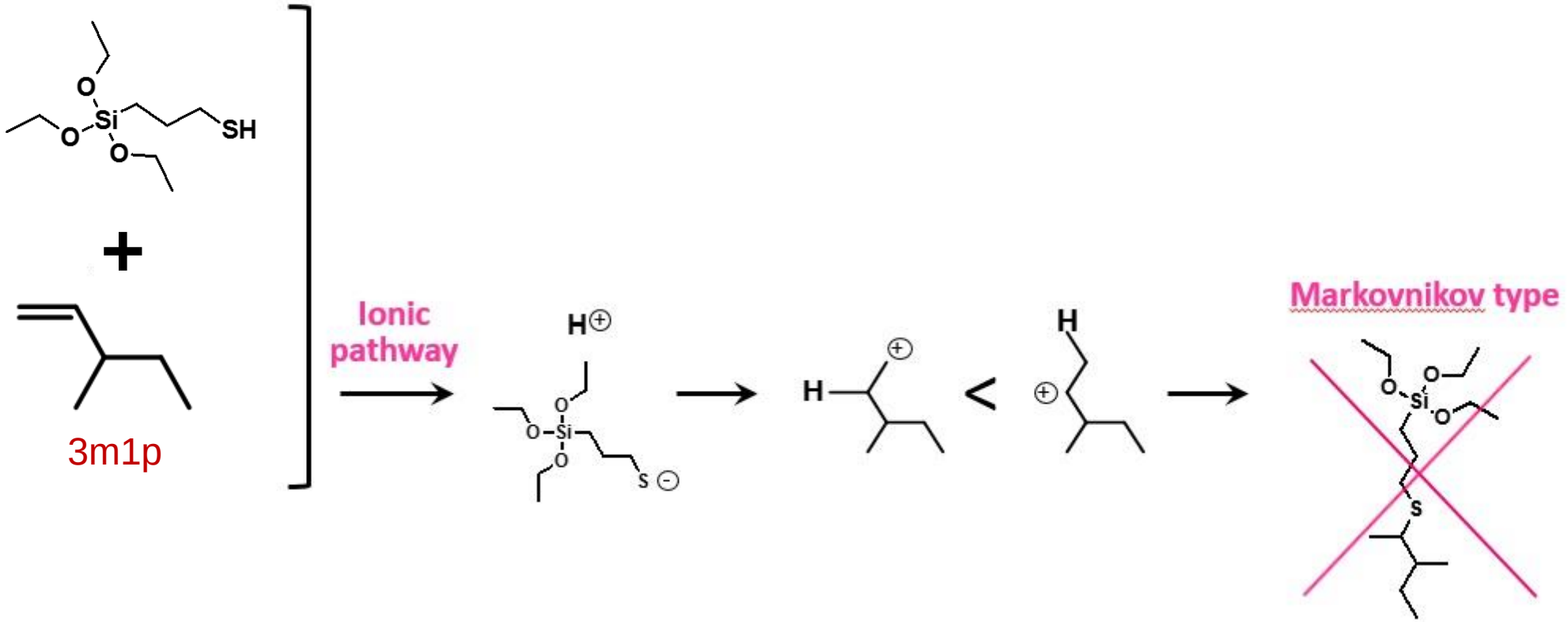


Confirmed by NMR

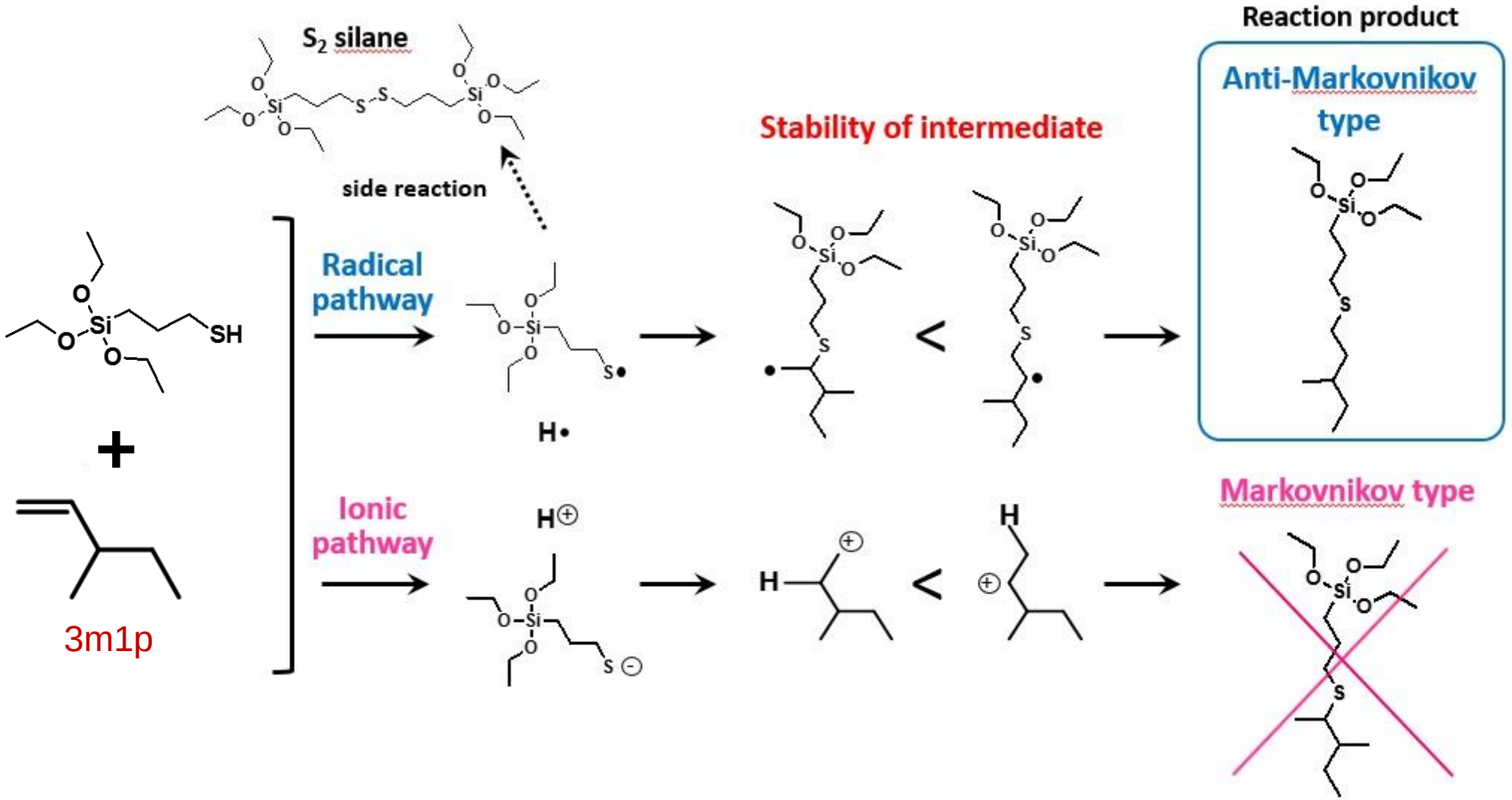
Vinyl-group in 3m1p couples to mercaptosilane:

Same reaction as in L-BR

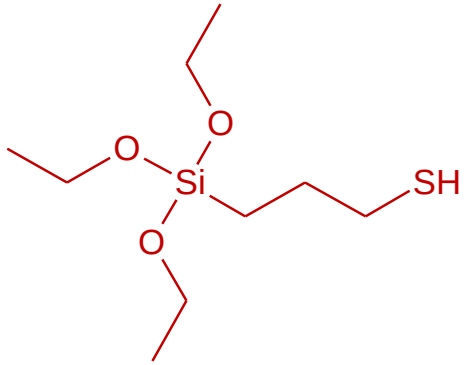
Possible reaction paths for vinyl olefin + mercaptosilane



Possible reaction paths for vinyl olefin + mercaptosilane



Model study with cis olefin in decane

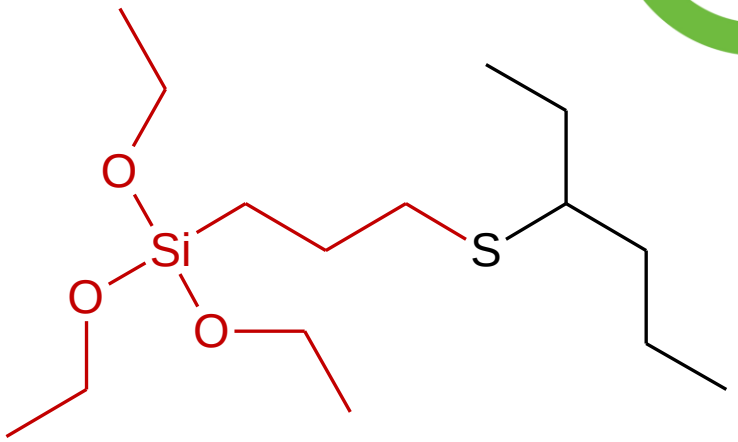


+

170°C

60 min

C3H

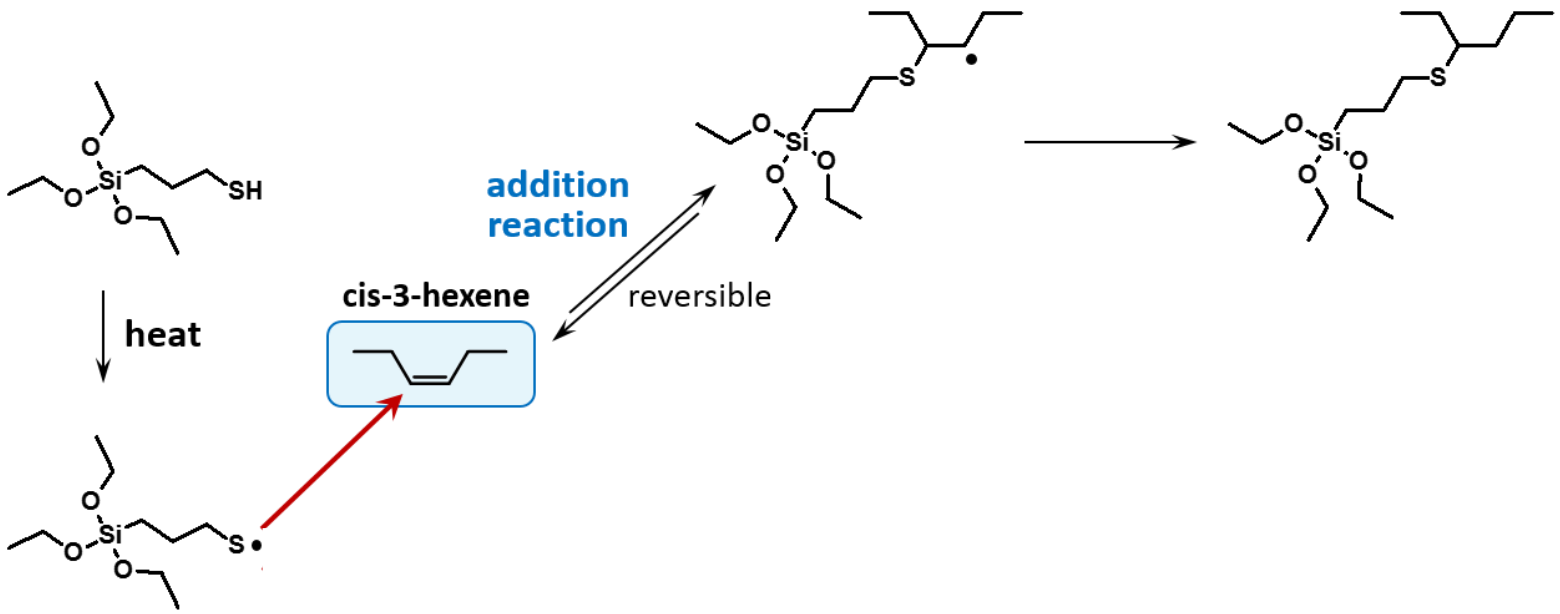


Confirmed by NMR

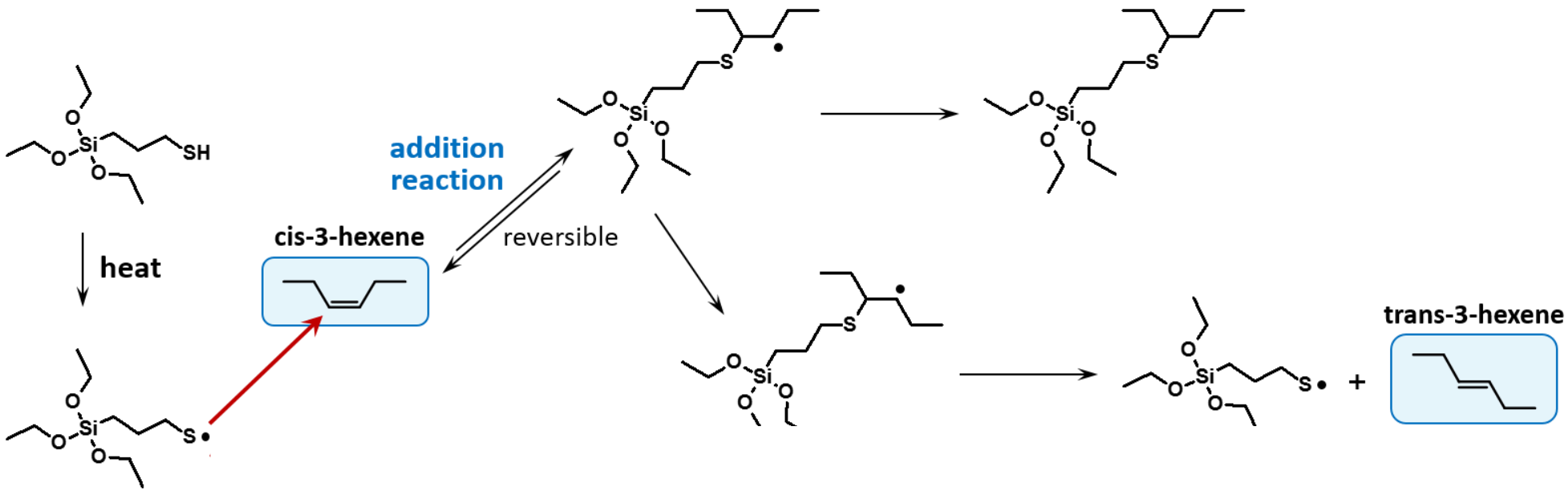
Cis-double bond in C3H couples to mercaptosilane:

- Same reaction as in L-BR
- Smaller yield than for vinyl olefin coupling

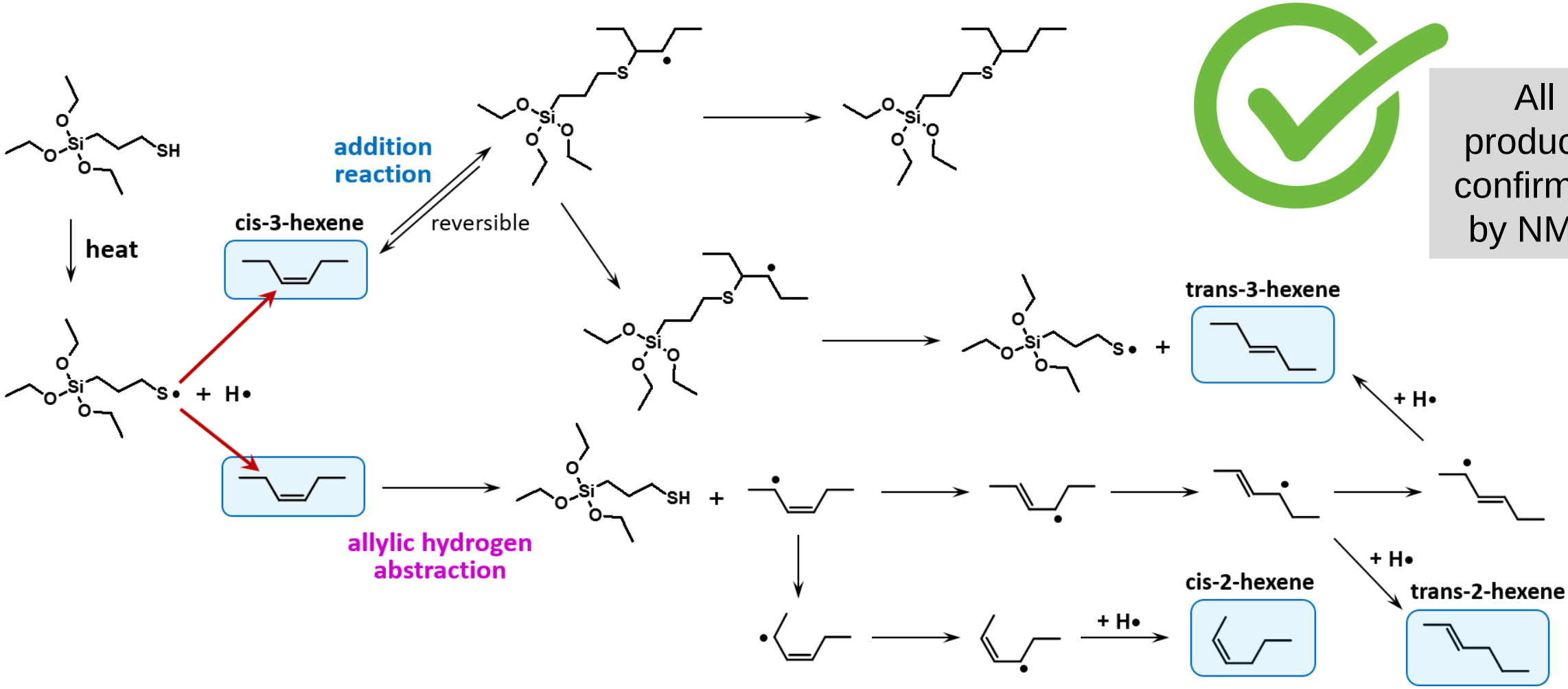
Possible reaction paths for cis olefin and mercaptosilane



Possible reaction paths for cis olefin and mercaptosilane



Possible reaction paths for cis olefin and mercaptosilane



All products confirmed by NMR

Model study
Results from olefin study

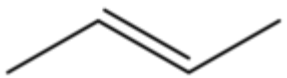
Does an early coupling towards double bonds in the polymer cause the processing issues of mercaptosilanes?

If so: Towards which double bond?

- Trans double bond does not couple to the thiol function.
- Cis- double bond and vinyl group can couple to the thiol function following a radical mechanism.
- Additionally, cis / trans isomerization can occur.

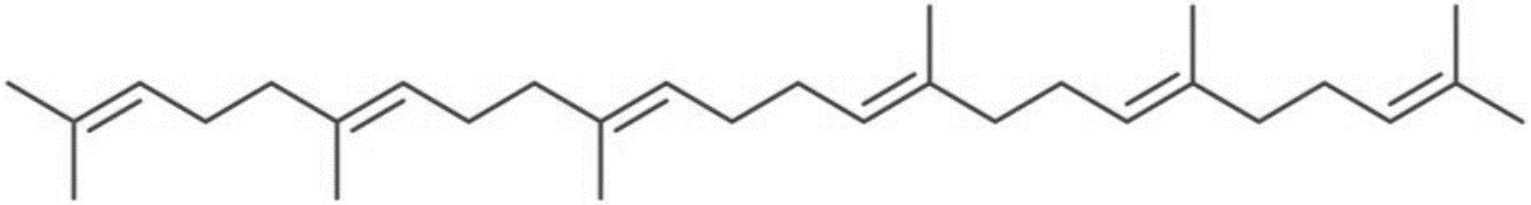
Do these couplings also take place in polymers?

Model study with polymeric-like molecules

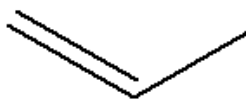


trans

=



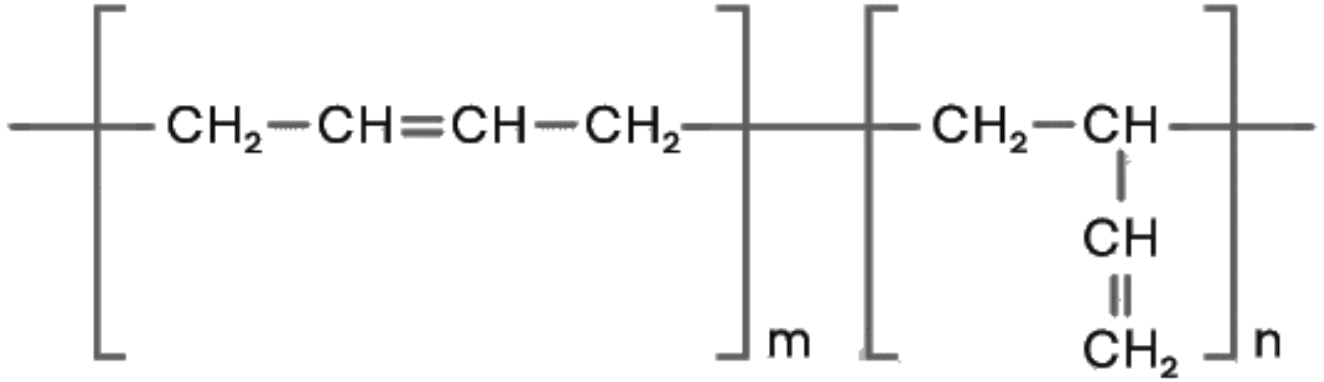
Squalene (100% trans)



vinyl

cis

=

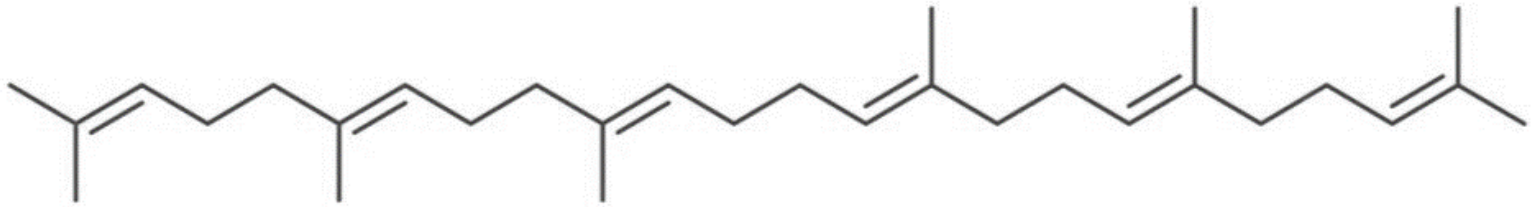


30% // 72% cis (and trans) 70% // 28% vinyl

High vinyl L-BR: Ricon® 156

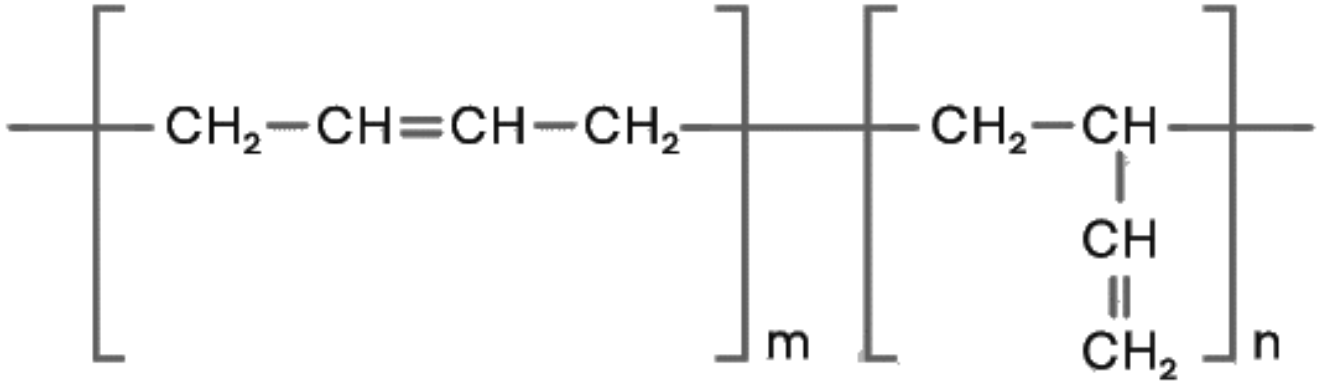
High cis L-BR Ricon® 130

Model study with liquid BR and squalene in decane



Squalene (100% trans)

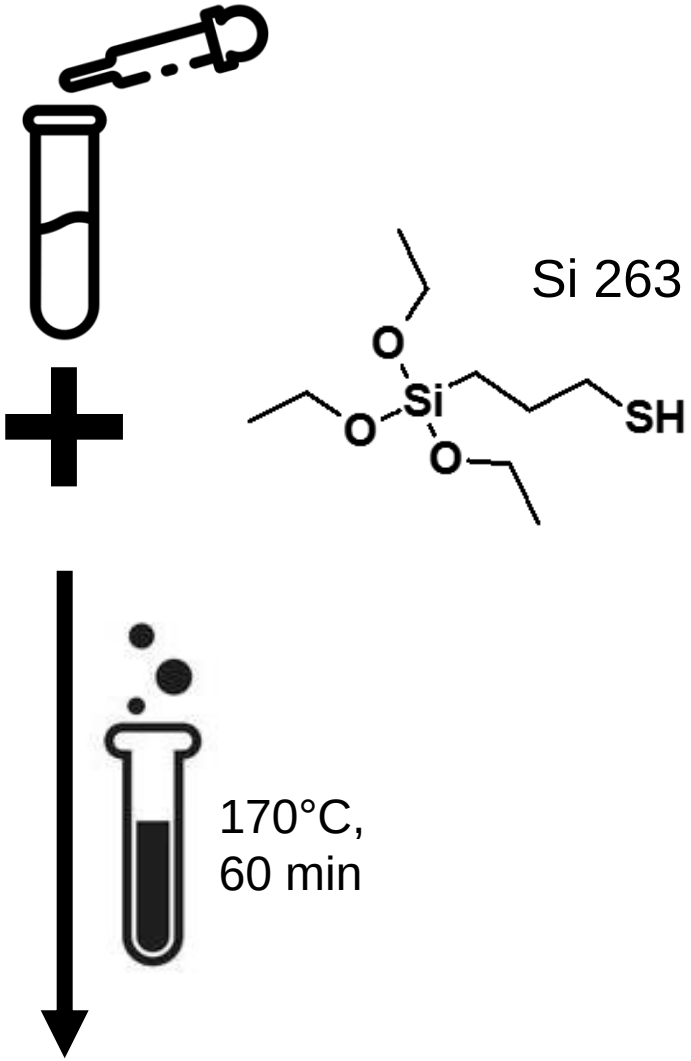
or



30% // 72% cis (and trans) 70% // 28% vinyl

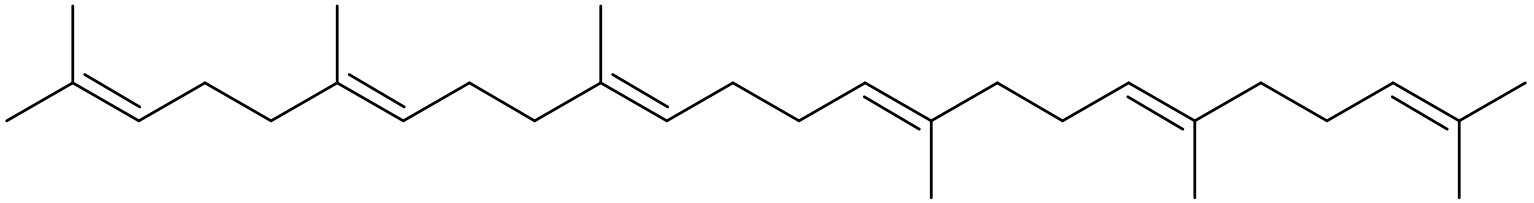
High vinyl L-BR: Ricon® 156

High cis L-BR Ricon® 130



Elastomer Technology and Engineering

Model study with squalene and mercaptosilane in decane

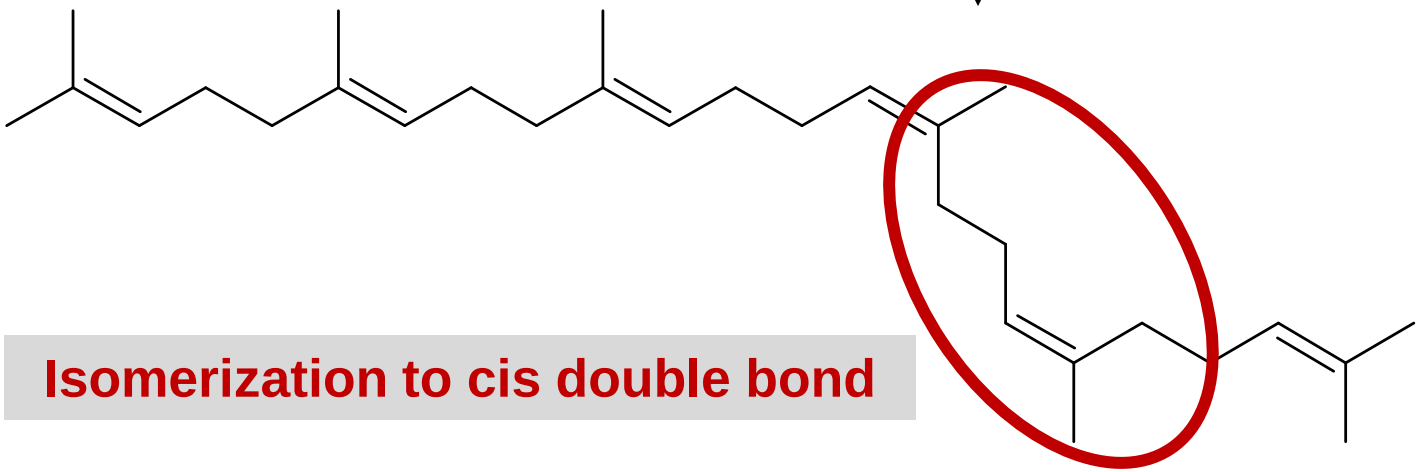


Confirmed by NMR

Squalene: trans doube bonds

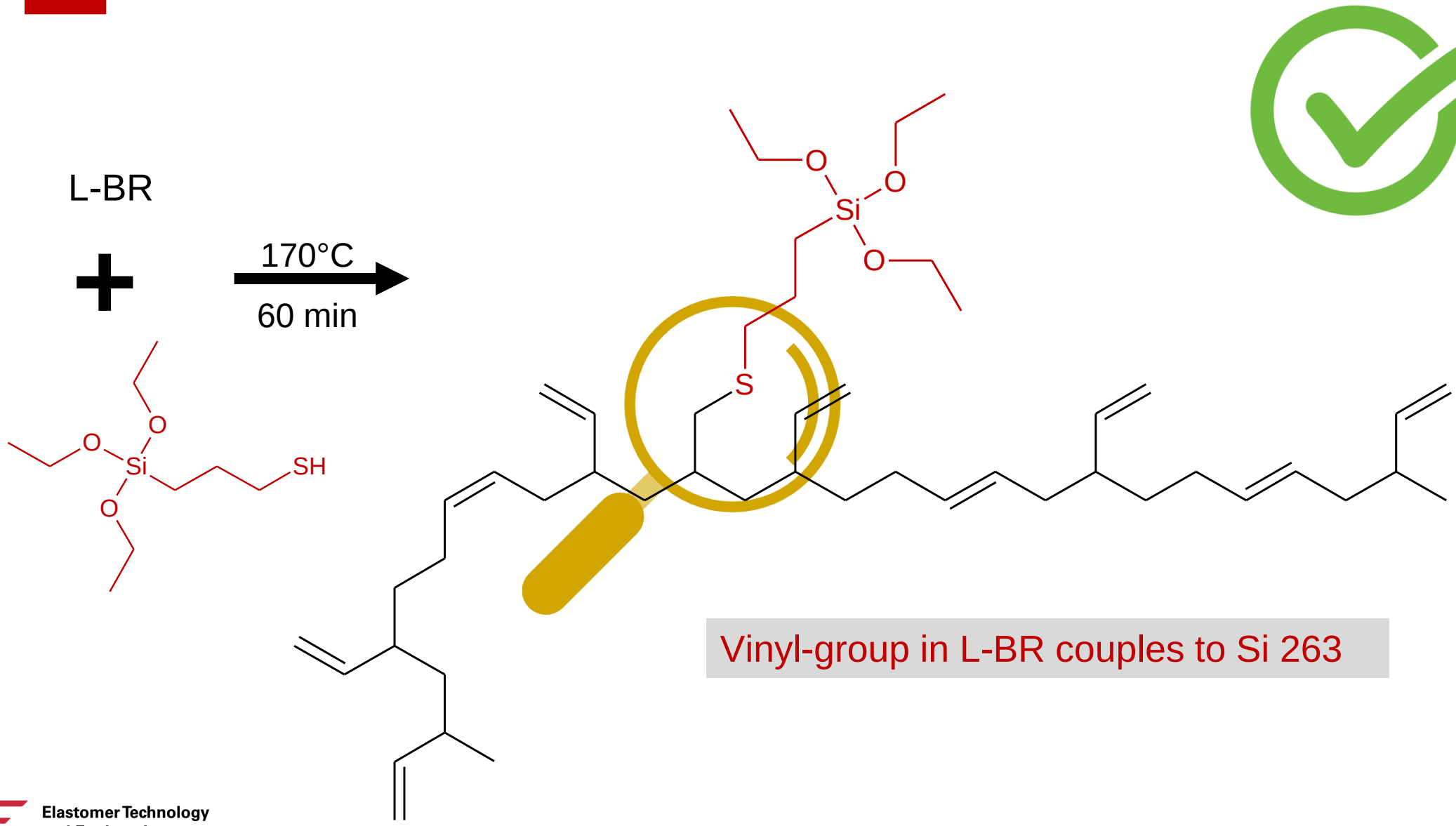
170°C, 60 min

No coupling reaction



Isomerization to cis double bond

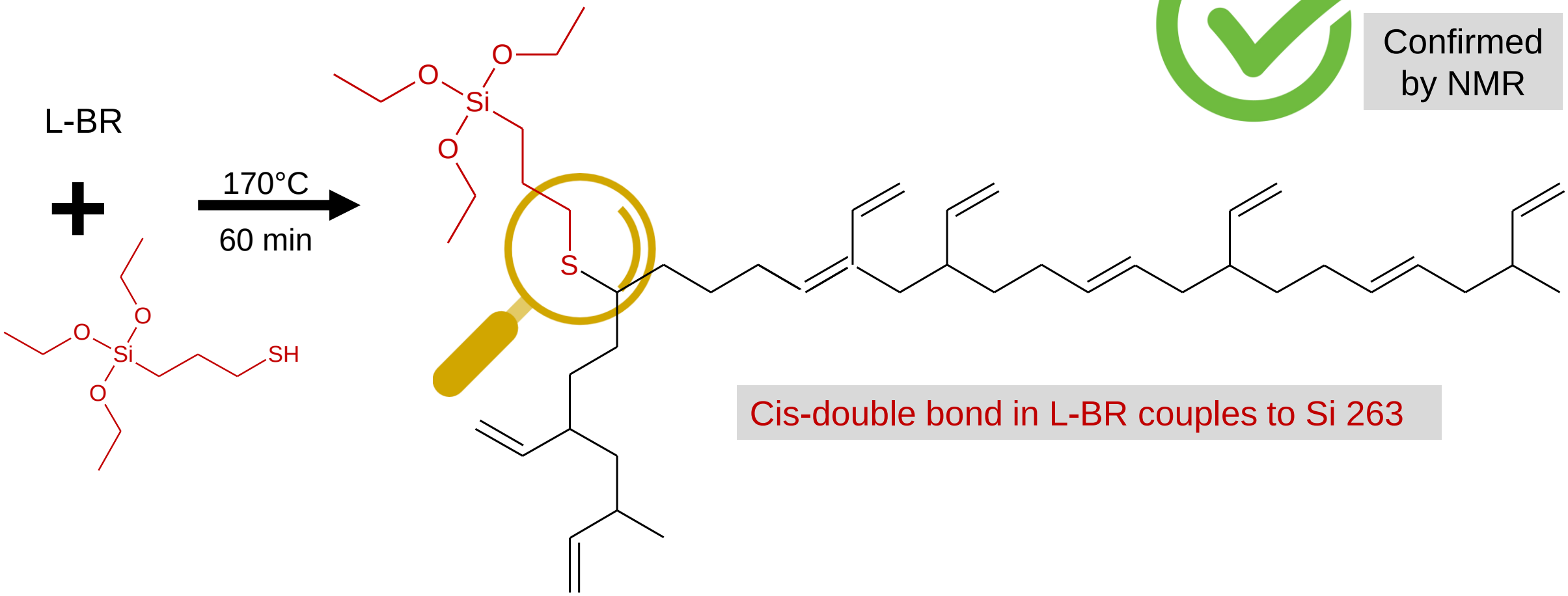
Model study with liquid BR and mercaptosilane in decane



Confirmed by NMR

Vinyl-group in L-BR couples to Si 263

Model study with liquid BR and mercaptosilane in decane



Confirmed by NMR

Cis-double bond in L-BR couples to Si 263

Model study
Results from olefin study

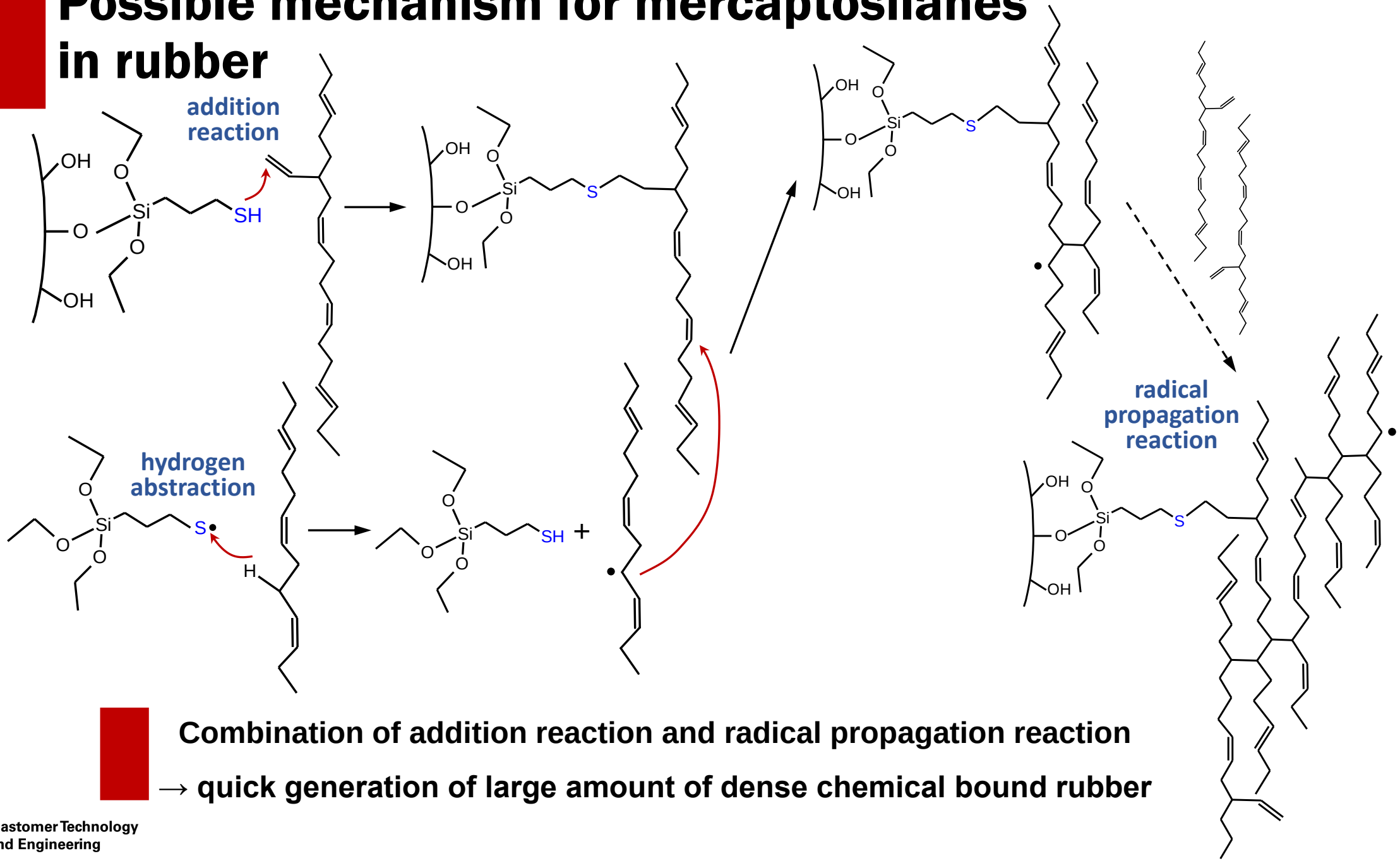
Does an early coupling towards double bonds in the polymer cause the processing issues of mercaptosilanes?

If so: Towards which double bond?

- Trans double bond does not couple to the thiol function.
- Cis- double bond and vinyl group can couple to the thiol function following a radical mechanism.
- Additionally, cis / trans isomerization can occur.

Do these couplings also take place in polymers? YES!

Possible mechanism for mercaptosilanes in rubber



Combination of addition reaction and radical propagation reaction

→ quick generation of large amount of dense chemical bound rubber

Summary

Mercaptosilanes + SSBR / BR:

- Isomerization of trans and cis double bonds
- Chemical reaction of –SH with vinyl or cis double bonds by radical mechanism

↓

leads to quick generation of a large amount of dense chemical bound rubber

↓

suppression of silica flocculation during vulcanization

↓

better dispersed silica

→ lower tanδ at 60°C value
= lower rolling resistance

↓

Formation of partly crosslinked rubber during mixing

→ worse processability

Solution to overcome processing issues

Mix Si 363® at low temperature (LT) in the first mixing stage

J. Kiesewetter, A. Hasse, Rubber World 131, September 2020, p. 30;
https://amican.com/there-is-always-a-solution/; J. da Silva, EngD thesis 2023

Solution to overcome processing issues

Green Tire tread compound based on:

- **SSBR / BR**
- **85 phr silica (ULTRASIL® 7000 and ULTRASIL® 9000)**
- **6.8 / 9 phr Si 363 ®**

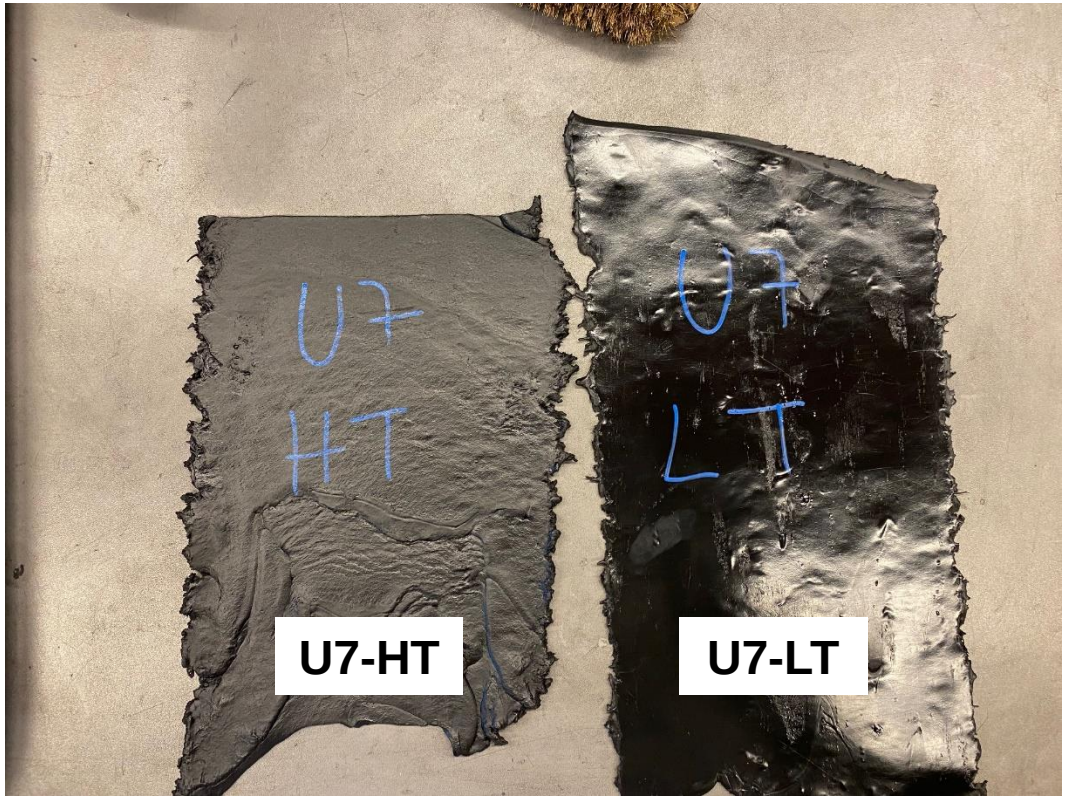
Dump temperature of 1st mixing stage:

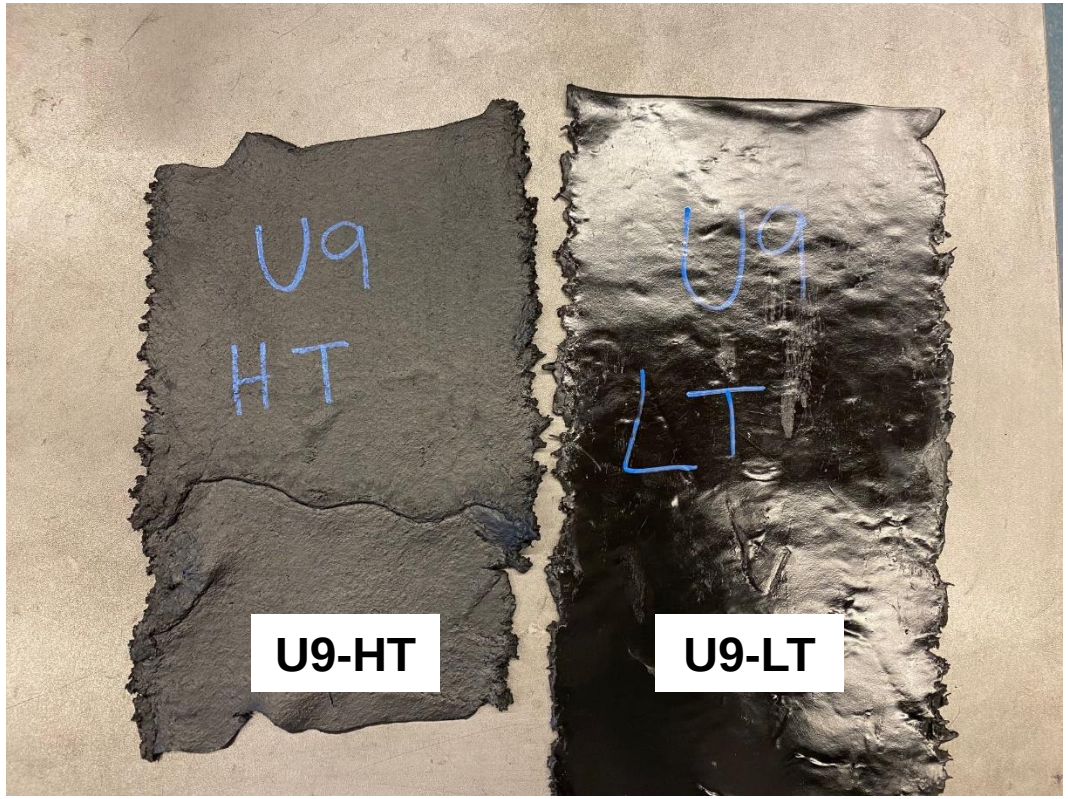
	High Temperature (HT)	Low Temperature (LT)
U7	156	117
U9	152	118

https://www.youtube.com/watch?app=desktop&v=3Fs3AjJquSY

Solution to overcome processing issues

Low temperature mixing – First stage

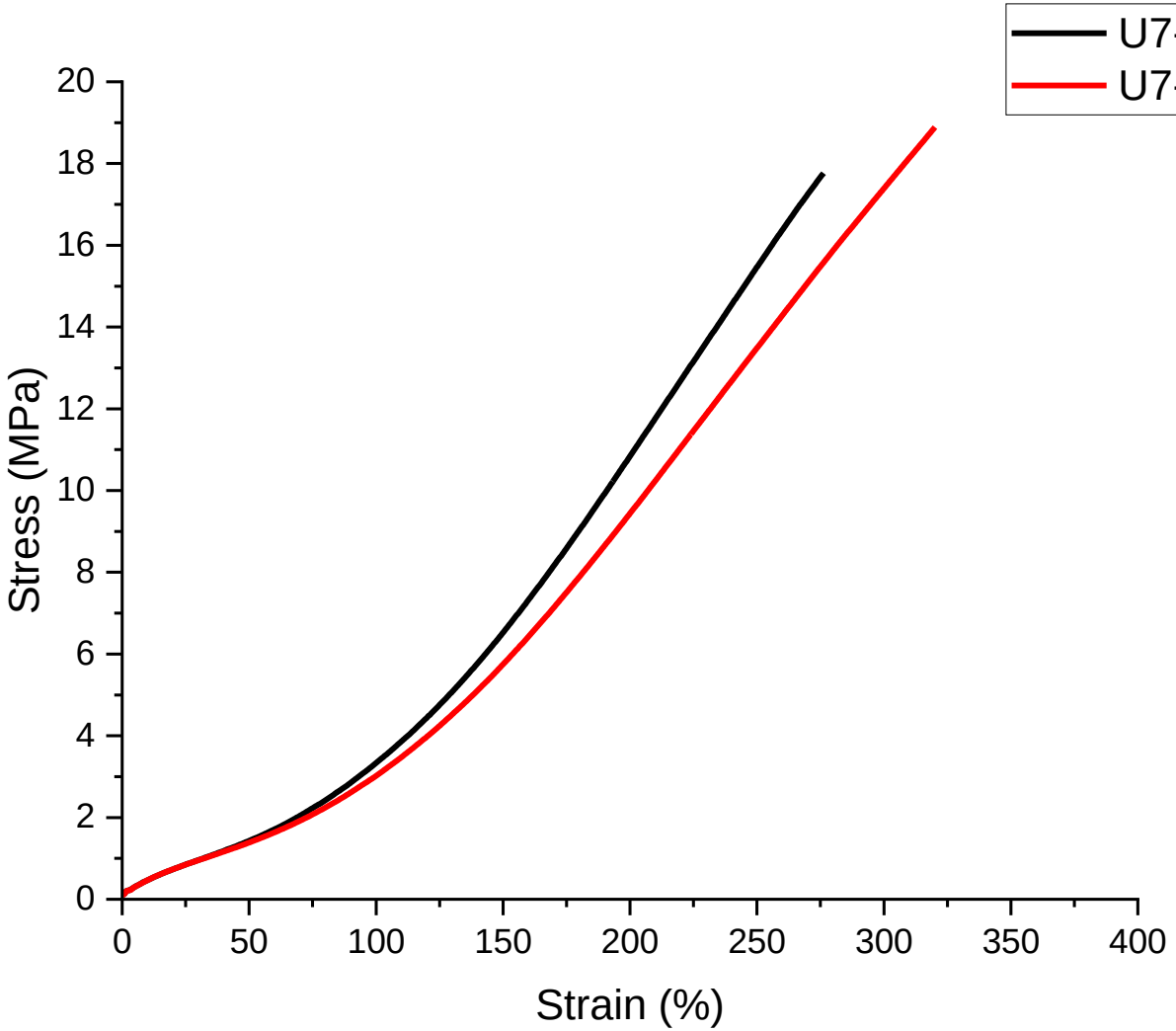


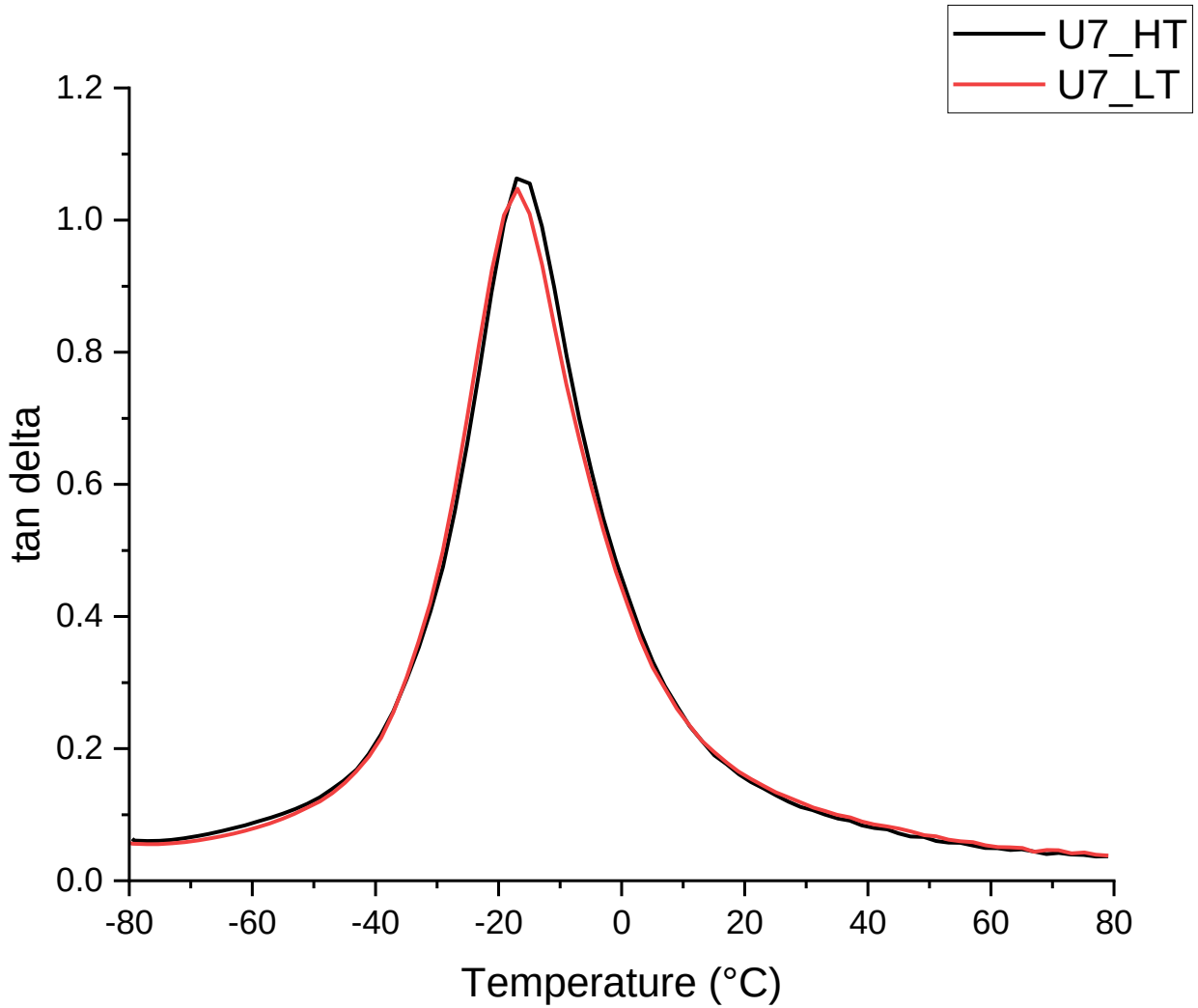


Highly improved sheet appearance for LT-mixed compounds

Solution to overcome processing issues

Stress-strain and DMA data of ULTRASIL 7000 filled tire tread compounds

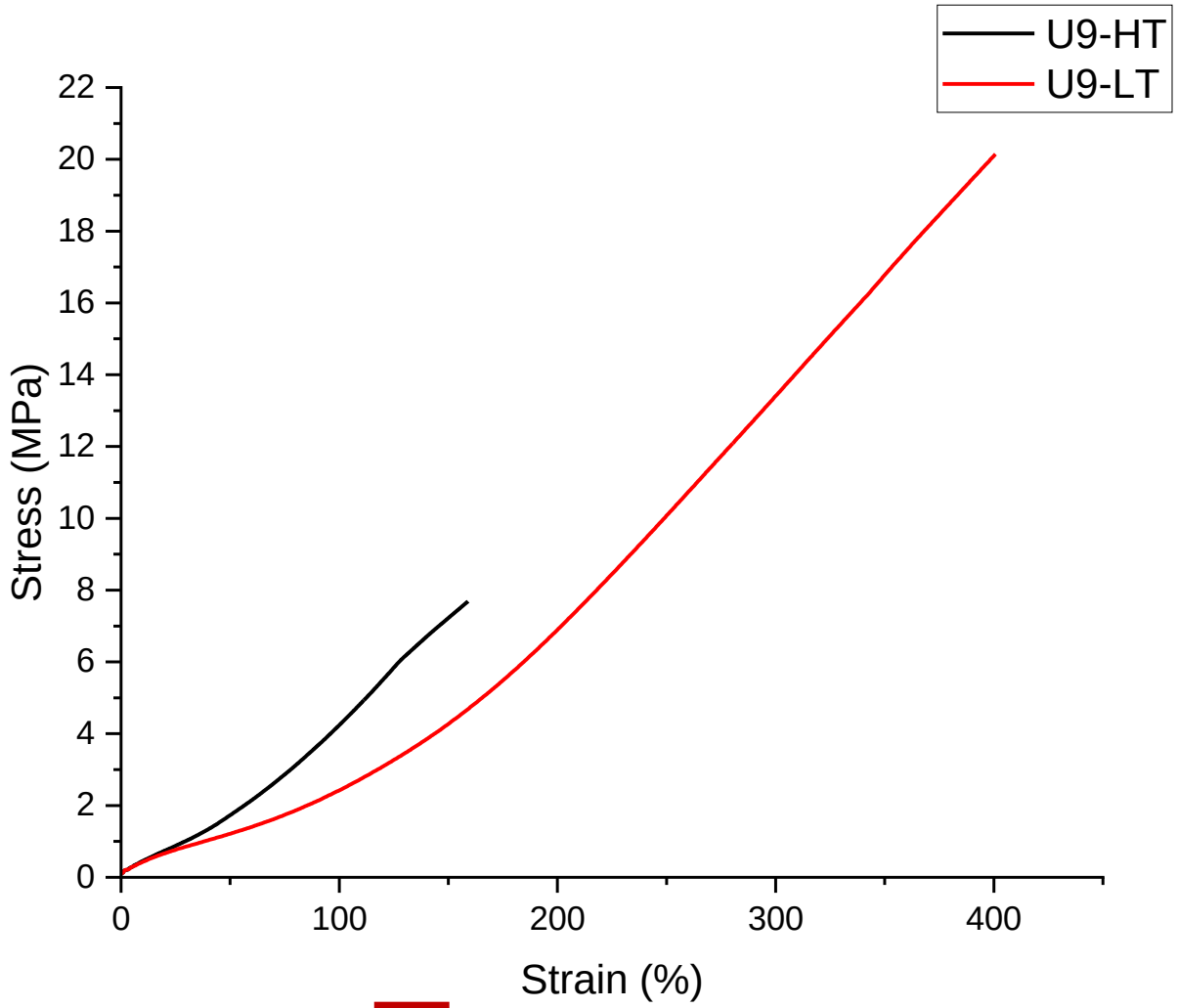


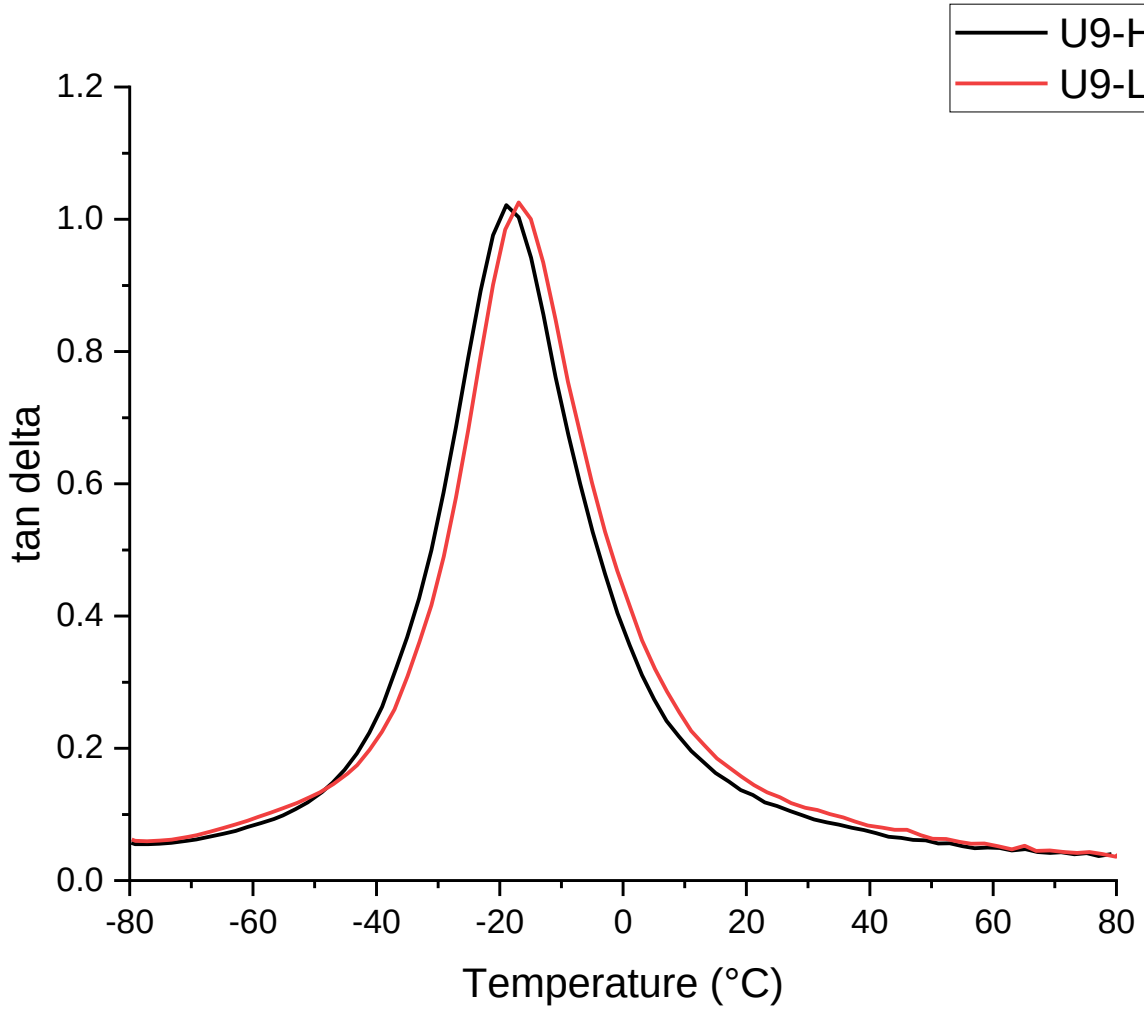


Slightly lower reinforcing but similar dynamic response for U7-LT compounds

Solution to overcome processing issues

Stress-strain and DMA data of ULTRASIL 9000 filled tire tread compounds





Incomplete silanization for high surface area silica U9-LT:

Lower reinforcing but quite similar dynamic response for U9-LT compounds

Summary

Coupling mechanism of mercaptosilanes further deciphered

Challenges during processing identified

Possible

https://amican.com/there-is-always-a-solution/

Thank you for your kind attention!