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3 July 2018,
Nuremberg, Germany

MIMICKING THE NATURE: HOOK-AND-LOOP ADHESION SYSTEMS FOR ELASTOMERS

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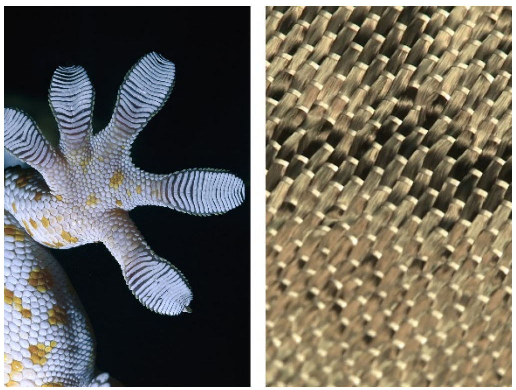
Deutsche Kautschuk-Tagung DKT 2018

ORIGIN OF CONCEPTS

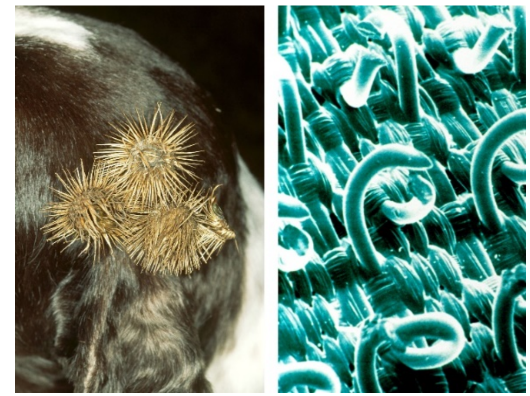
WHERE DO IDEAS COME FROM? – BIOMIMICRY: CASE STUDY

Gecko Feet Adhesives



Shark skin

Velcro



Annoying feature of weeds

Useful technical solutions

https://www.bloomberg.com/news/photo-essays/2015-02-23/14-smart-inventions-inspired-by-nature-biomimicry

INTRODUCTION

CHARACTERISTICS OF MICROSCOPIC VS. MOLECULAR VELCRO SYSTEMS

VS.

Microscopic Velcro system

- Superior fatigue resistence
- Superior reconnectability performance
- Good mechanical properties
- Good ageing resistance
- Stiff hooks, elastic loops
- Hooks and loops materials chemical compatibility – not relevant
- Molecular mobility – not relevant

Molecular Velcro system

- Superior fatigue resistence
- Superior reconectability performance
- Good mechanical properties
- Good ageing resistance
- Stiff/elastic hooks, stiff/elastic loops
- Hooks and loops materials chemical compatibility – very relevant (mutual solubility/miscibility)
- Molecular mobility – very relevant

INTRODUCTION

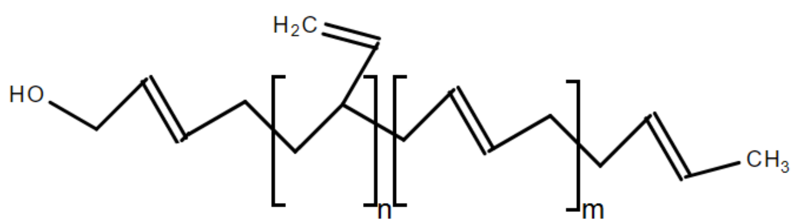
FOCUS ON PHYSICAL INTERACTIONS

Chemical interactions:
- Covalent bonds
- Ionic bonds
- Coordinate bonds

Strong physical interactions:
- Hydrogen bonds
- Ion/dipole and ion-induced/dipole interactions
- Dipole/dipole interactions

Physical interactions:
- Dispersion interactions
- Steric hindrance
- Macromolecular entanglements
- Chemical affinity (miscibility/solubility)

Velcro-like approach – grafting of relatively large molecules onto the silica surface of good chemical affinity to the rubber, enhancing interactions *via* physical entanglements and steric hindrance.



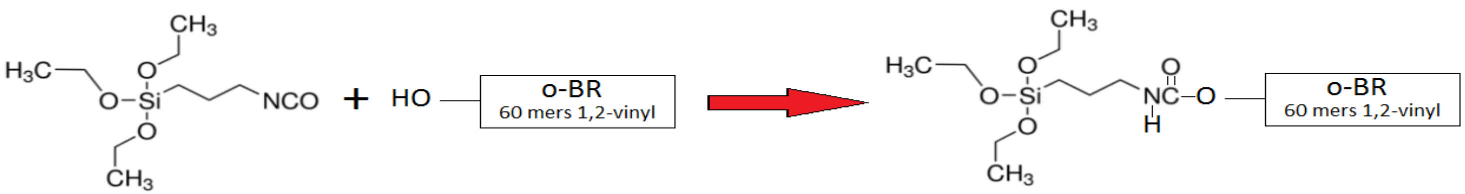
Molecular weight of the o-BR: **4691 g/mol**
Length of straightened molecule: **~30 nm**
Number of vinyl mers: **~60 per molecule**

Telechelic mono-hydroxy polybutadiene oligomer (o-BR) was used as a backbone for the modifier.

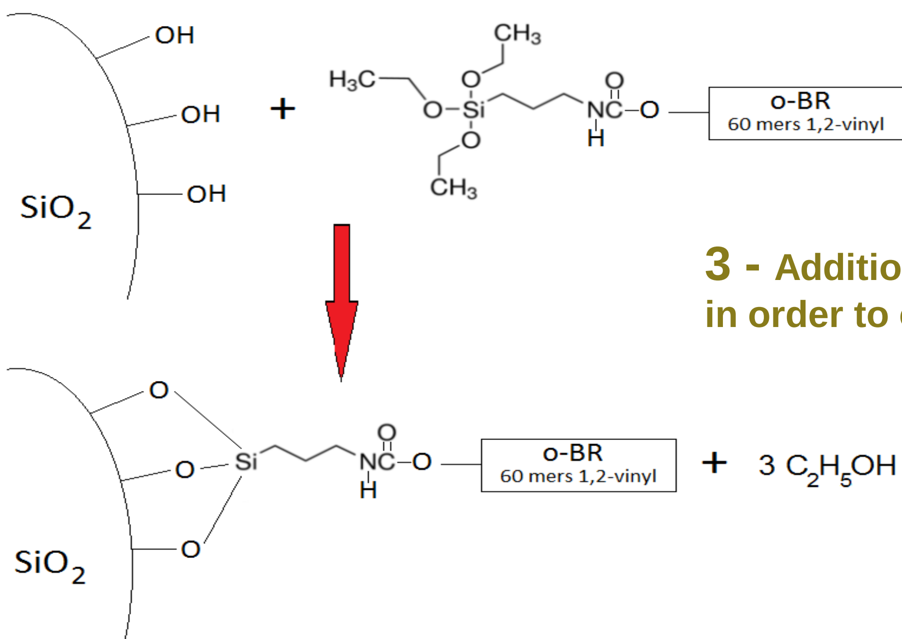
INTRODUCTION

SCHEME OF SILICA-SURFACE MODIFICATION

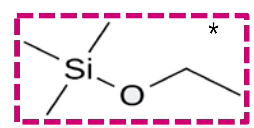
1 – Attaching the isocyanate silane molecule to the telechelic o-BR chain



2 – Grafting on the silica surface



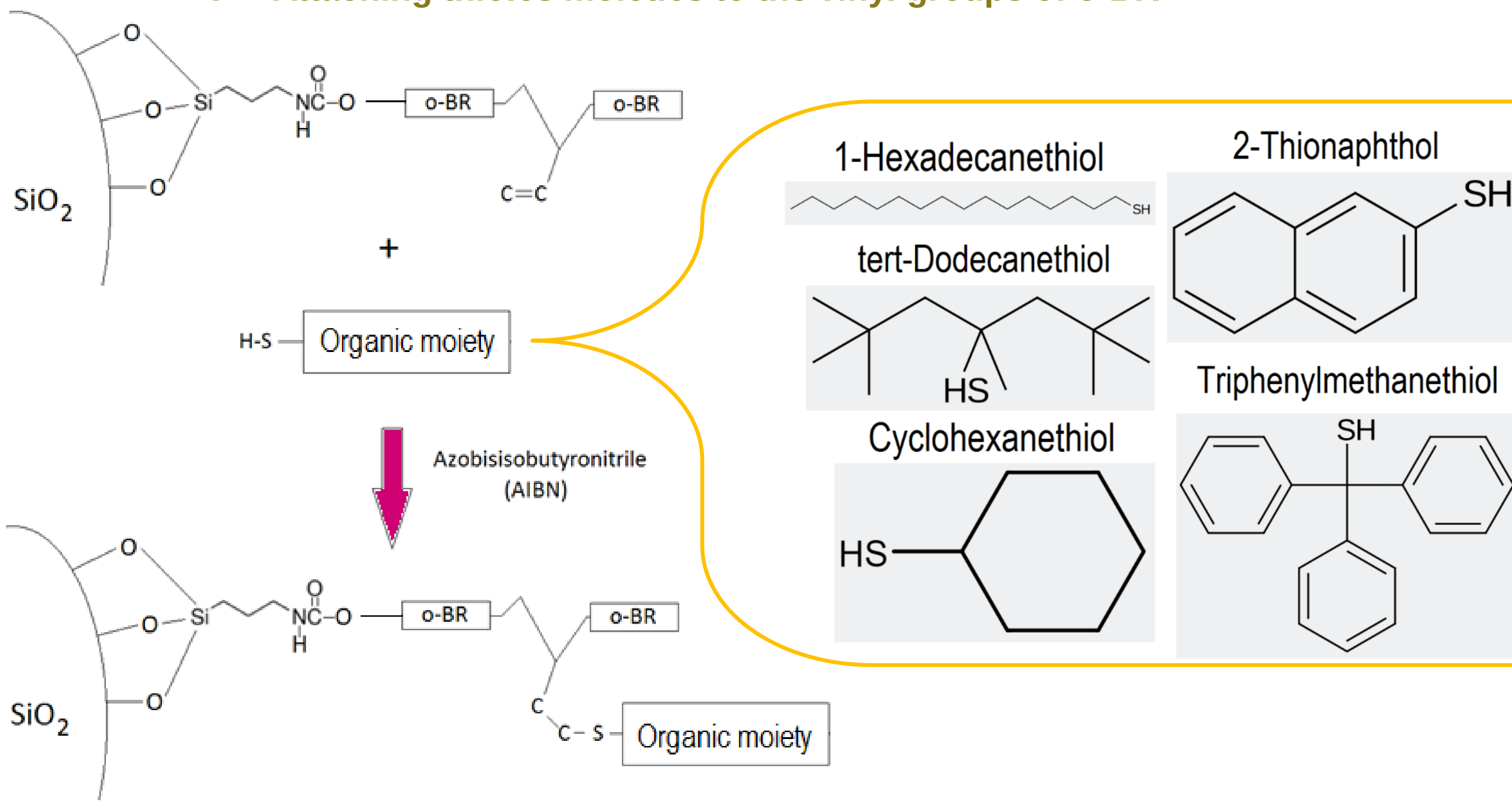
3 - Additional treatment with trimethylethoxysilane in order to cover residual, reactive silanol groups



INTRODUCTION

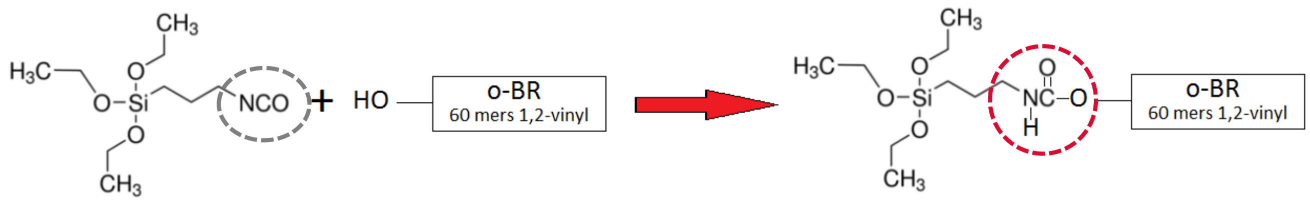
SCHEME OF SILICA-SURFACE MODIFICATION

4 – Attaching thioles moieties to the vinyl groups of o-BR

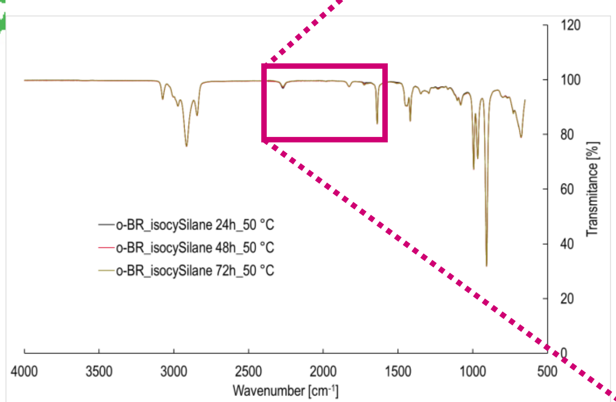


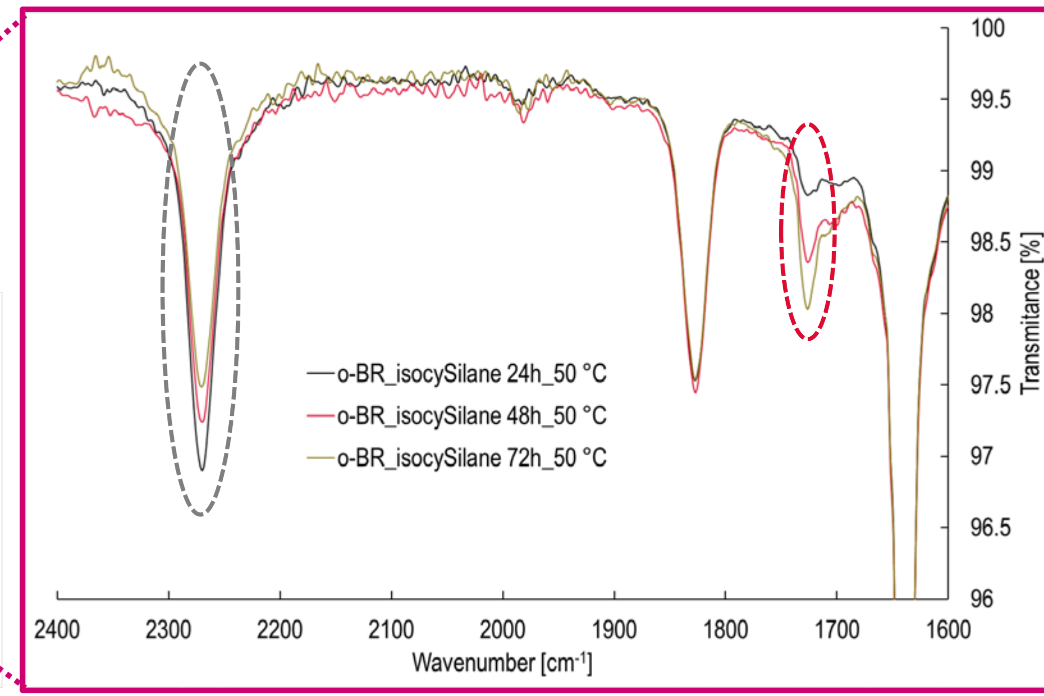
SYNTHESIS OF OLIGOMER-BACKBONE

REACTION PROGRESS TRACKING BY FTIR

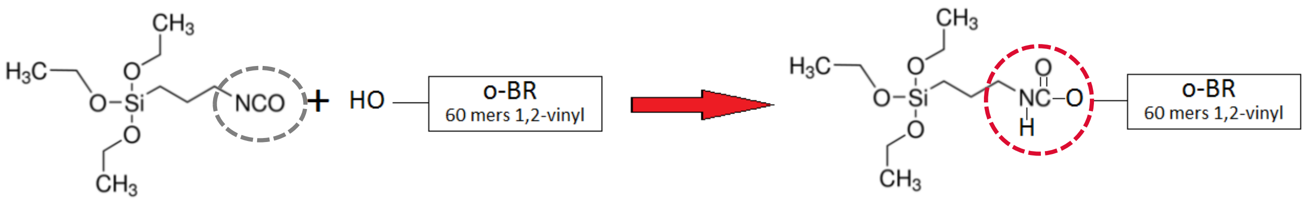


Isocyanate silane – 0.527 g + o-BR – 10 g: mixed together and heated at 50 °C for 24, 48 and 72 hours.

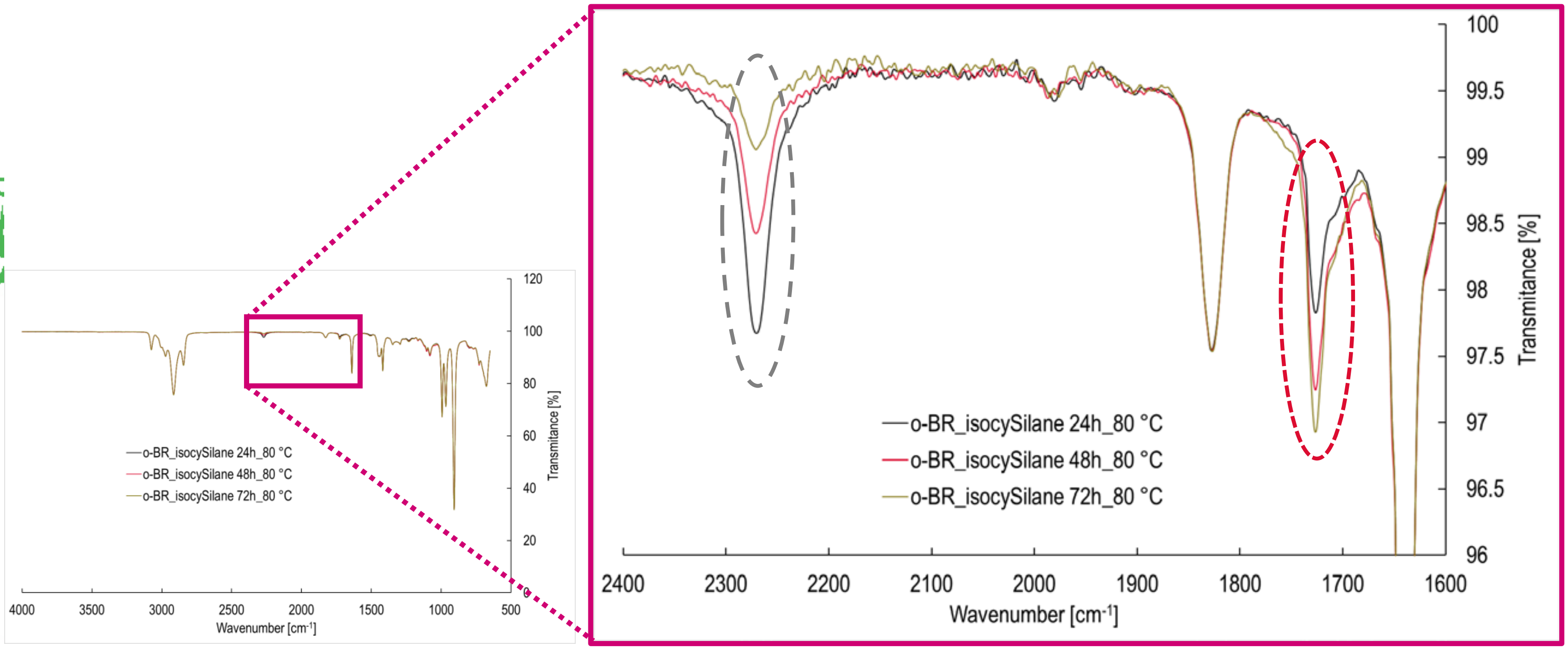




SYNTHESIS OF OLIGOMER-BACKBONE
REACTION PROGRESS TRACKING BY FTIR



Isocyanate silane – 0.527 g + o-BR – 10 g: mixed together and heated at 80 °C for 24, 48 and 72 hours.



SYNTHESIS OF OLIGOMER-BACKBONE

REACTION PROGRESS TRACKING BY FTIR

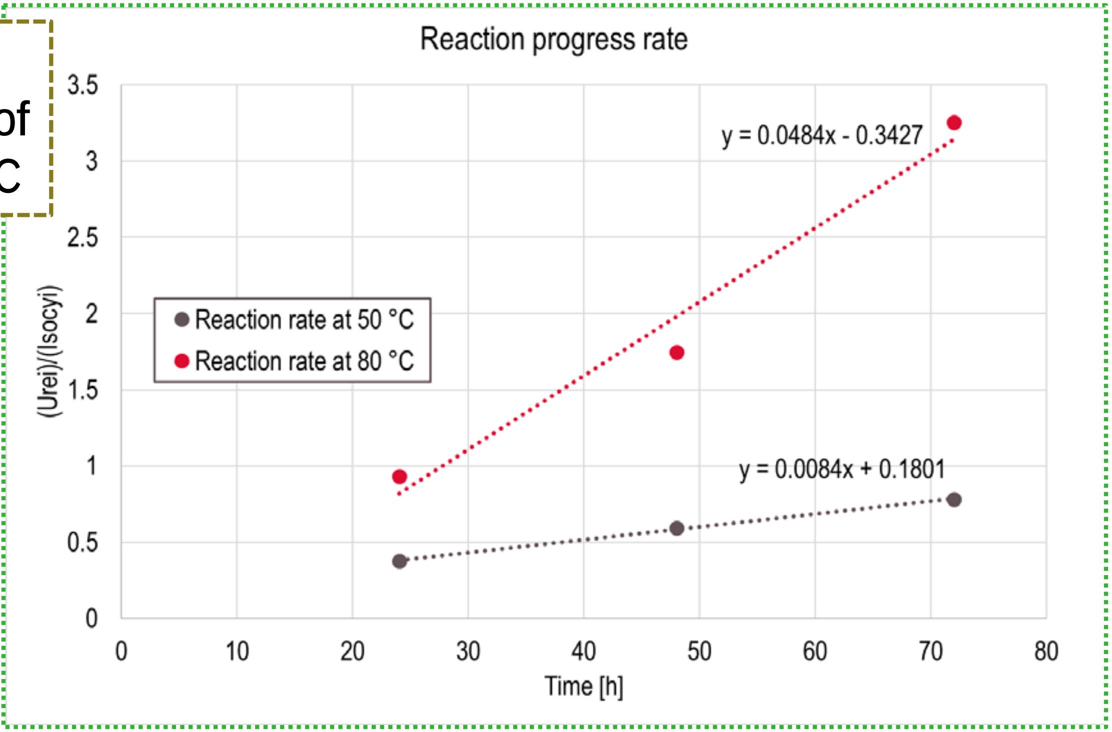
Reaction rate at 50 °C

Time [h]	Isocyanate group intensity ($Isocy_i$)	Urethane group intensity (Ure_i)	(Ure_i)/($Isocy_i$)
24	3.0999	1.1704	0.3775
48	2.7610	1.6400	0.5940
72	2.5133	1.9654	0.7820

Reaction rate at 80 °C

Time [h]	Isocyanate group intensity ($Isocy_i$)	Urethane group intensity (Ure_i)	(Ure_i)/($Isocy_i$)
24	2.3247	2.1735	0.9350
48	1.5761	2.7515	1.7458
72	0.9432	3.0720	3.2569

The reaction rate increases significantly with the increase of temperature from 50 °C to 80 °C

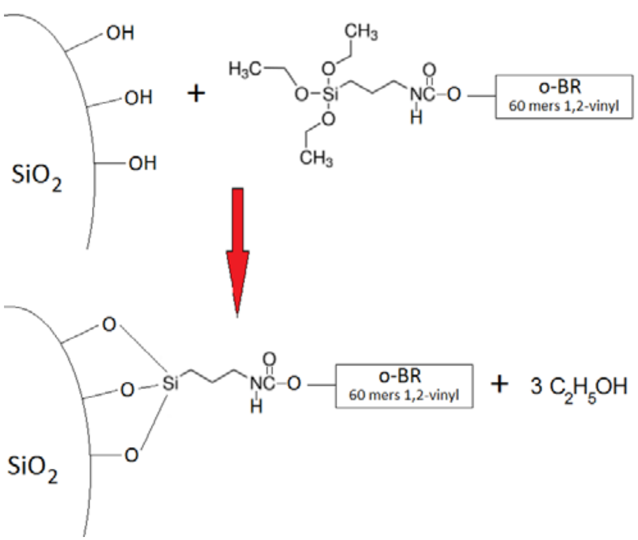


OLIGOMER-BACKBONE GRAFTING ON SILICA SURFACE

PROCEDURE CHARACTERISTICS

Composition of the samples

Sample description	Weight ratio	Precipitated silica (MP)	IsocySilane/o-BR
Silica + 20 silane_o-BR_extr20h	*1/5*	*100 g*	*20 g*
Silica + 50 silane_o-BR_extr20h	*1/2*	*100 g*	*50 g*
Silica + 100 silane_o-BR_extr20h	*1/1*	*50 g*	*50 g*



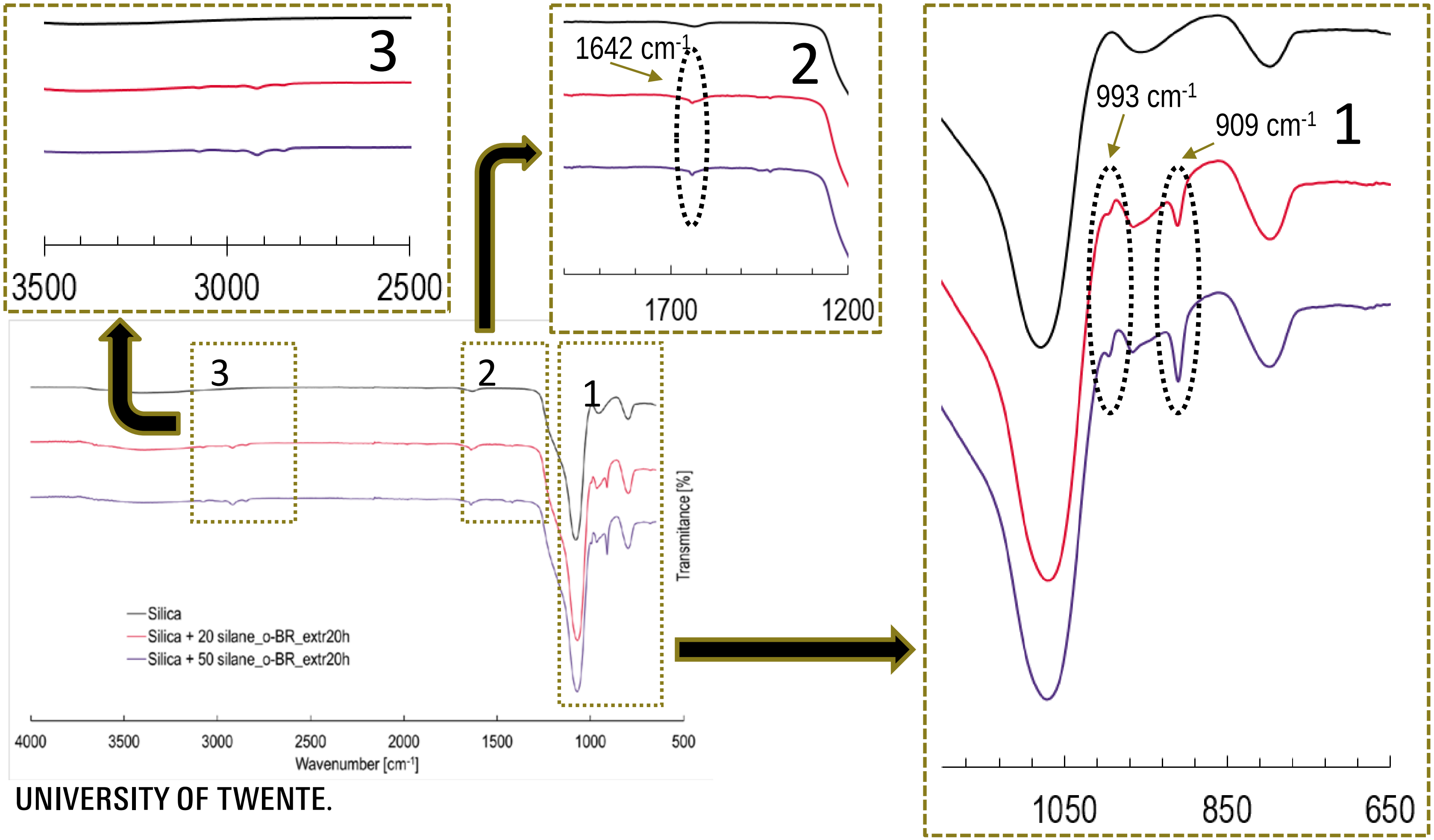
Procedure:

- Duration - 24 hours
- Air atmosphere
- Temperature - 100 °C
- Mechanical stirring – 150 rpm
- Extraction in toluene after the reaction – 20 hours

OLIGOMER-BACKBONE GRAFTING ON SILICA SURFACE

GRAFTING RESULTS ANALYSED BY FTIR

FTIR spectra of silica modified with various amounts of the oligomer-backbone *(indicated bands from unsaturated groups)*

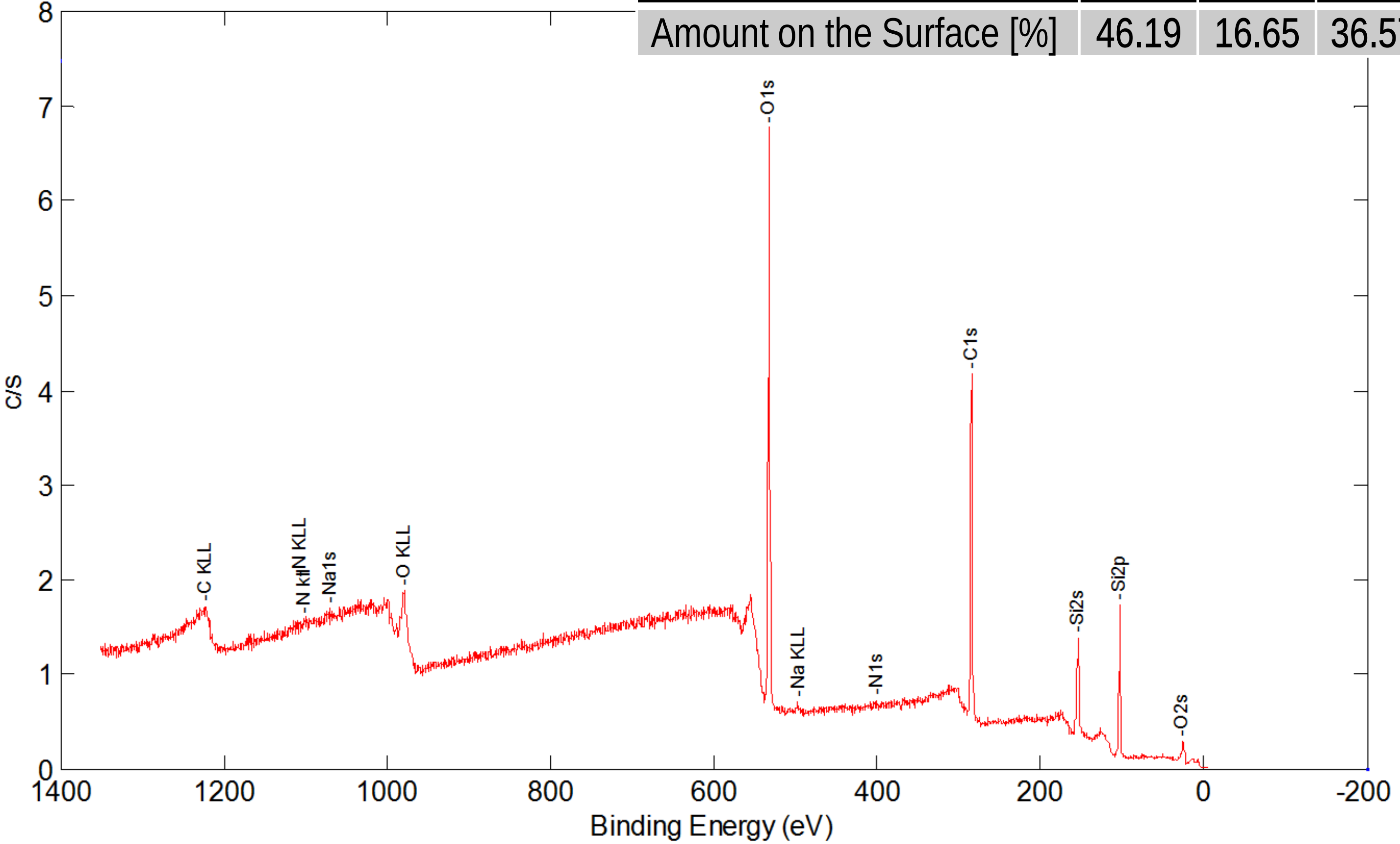


OLIGOMER-BACKBONE GRAFTING ON SILICA SURFACE

GRAFTING RESULTS ANALYSED BY XPS

*XPS analysis of the silica sample modified with **50 parts** of the o-BR per 100 parts of the silica*

Element	*C*	*Si*	*O*	*Na*	*N*
Amount on the Surface [%]	46.19	16.65	36.57	0.40	0.19



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OLIGOMER-BACKBONE GRAFTING ON SILICA SURFACE

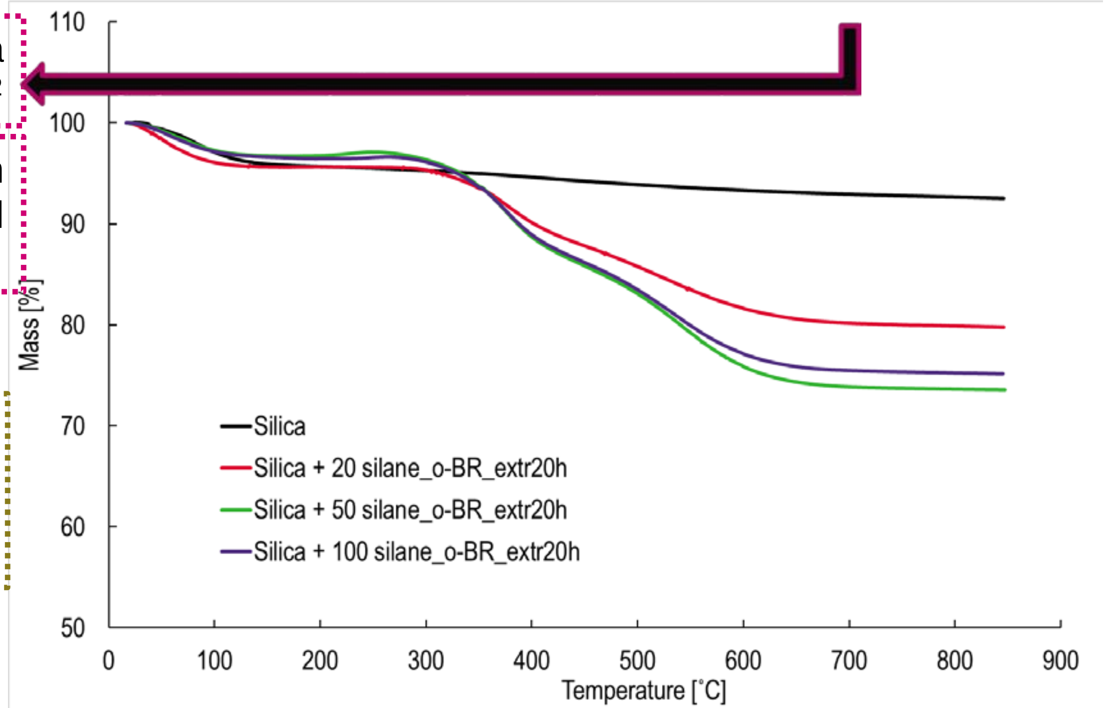
GRAFTING RESULTS ANALYSED BY TGA

Sample description	Summary mass loss [%]	Mass loss of organic component [%]	Density of grafted molecules [1/nm^2]
Silica	*7.5*	-	-
Silica + 20 silane_o-BR_extr20h	*20.2*	*15.8*	*6.37*
Silica + 50 silane_o-BR_extr20h	*26.4*	*22.9*	*4.07*
Silica + 100 silane_o-BR_extr20h	*24.8*	*21.3*	*4.46*

Average silanol group concentration on silica surface according to literature is ~5 -OH/nm^2

Single o-BR molecule terminated with the silane can react with up to 3 silanol groups (ca. 10-15 % of all -OH groups)

Additional treatment is required to cover the residual, reactive -OH groups



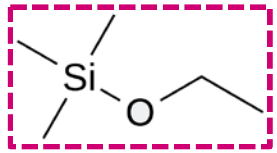
L. T. Zhuravlev (2000): The surface chemistry of amorphous silica. Zhuravlev model, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 173:1-3, 1-38, DOI: 10.1016/S0927-7757(00)00556-2

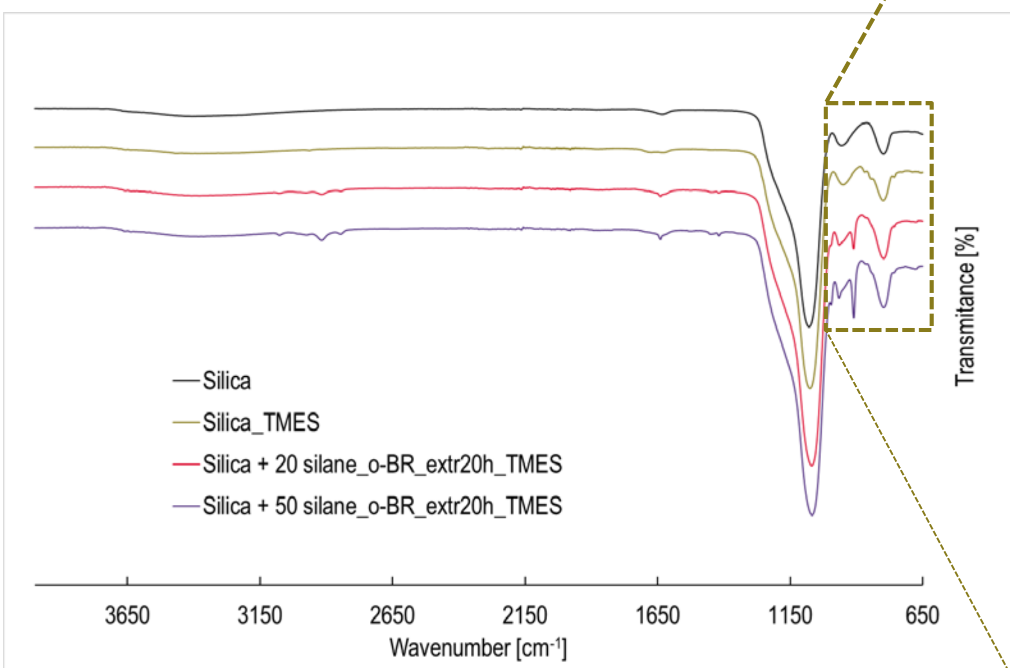
ADDITIONAL SILANIZATION

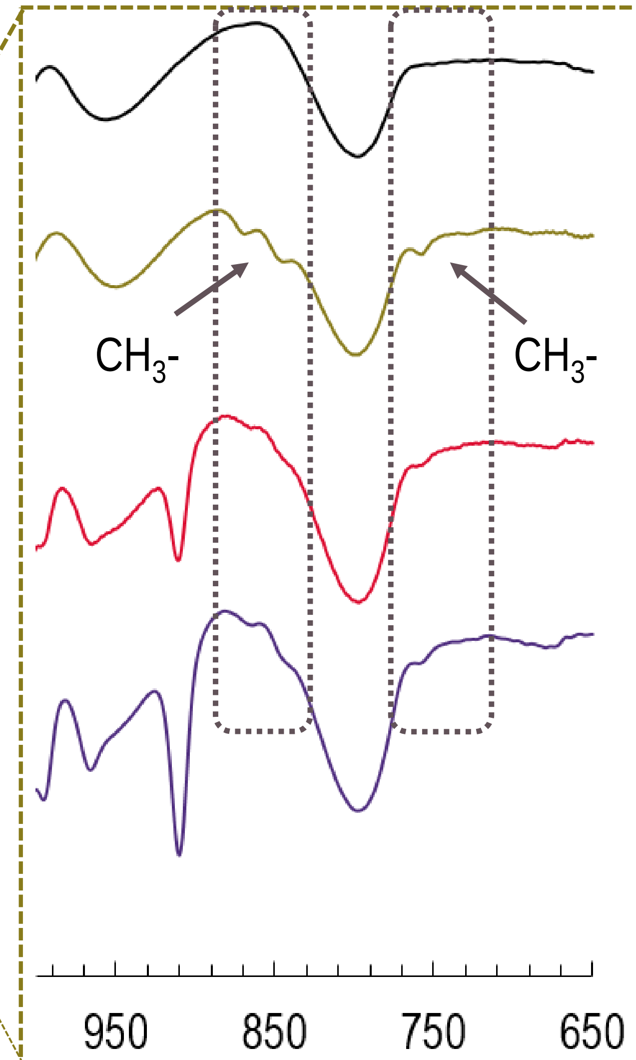
SILANIZATION RESULTS ANALYSED BY FTIR

Additional treatment with trimethylethoxysilane in order to cover residual, reactive silanol groups.

- Suspension in toluene
- Temperature: 70 °C
- Duration: 24 hours



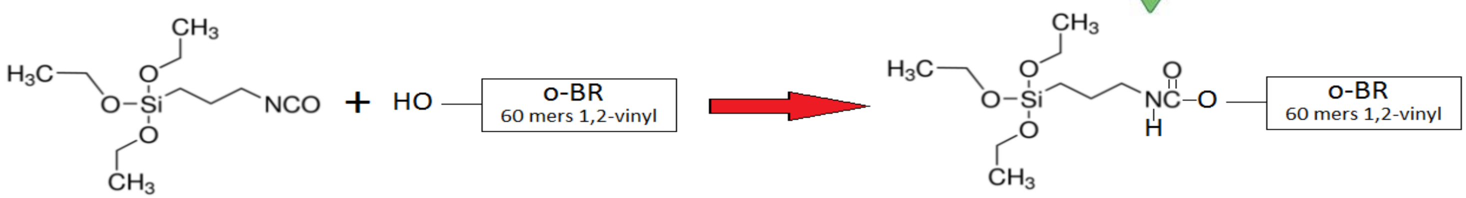




PROGRESS OF THE MODIFICATION

SCHEME OF SILICA-SURFACE MODIFICATION

1 – Attaching the silane molecule to the telechelic o-BR chain



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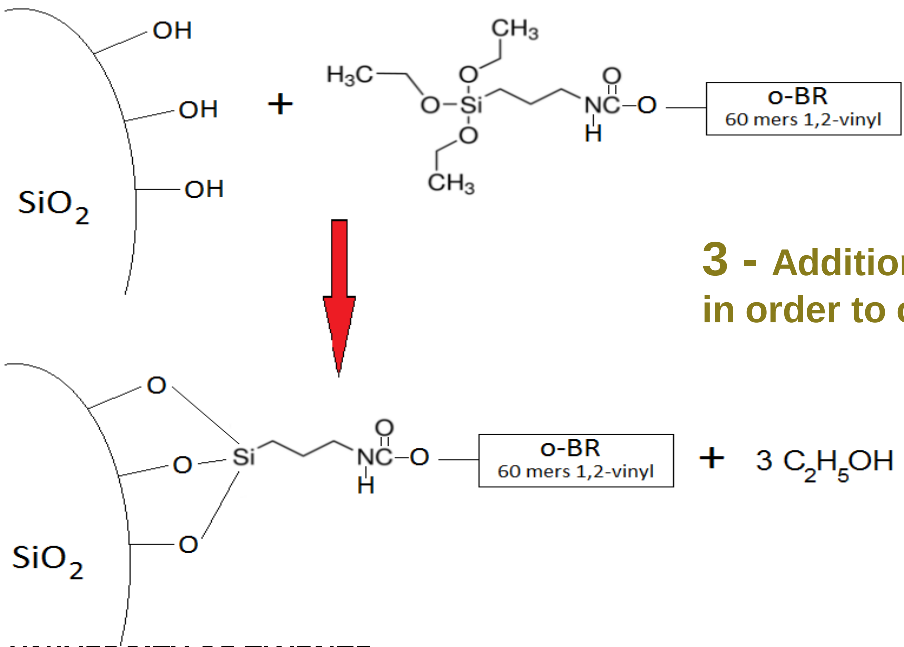
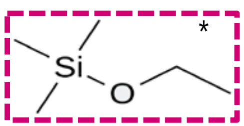


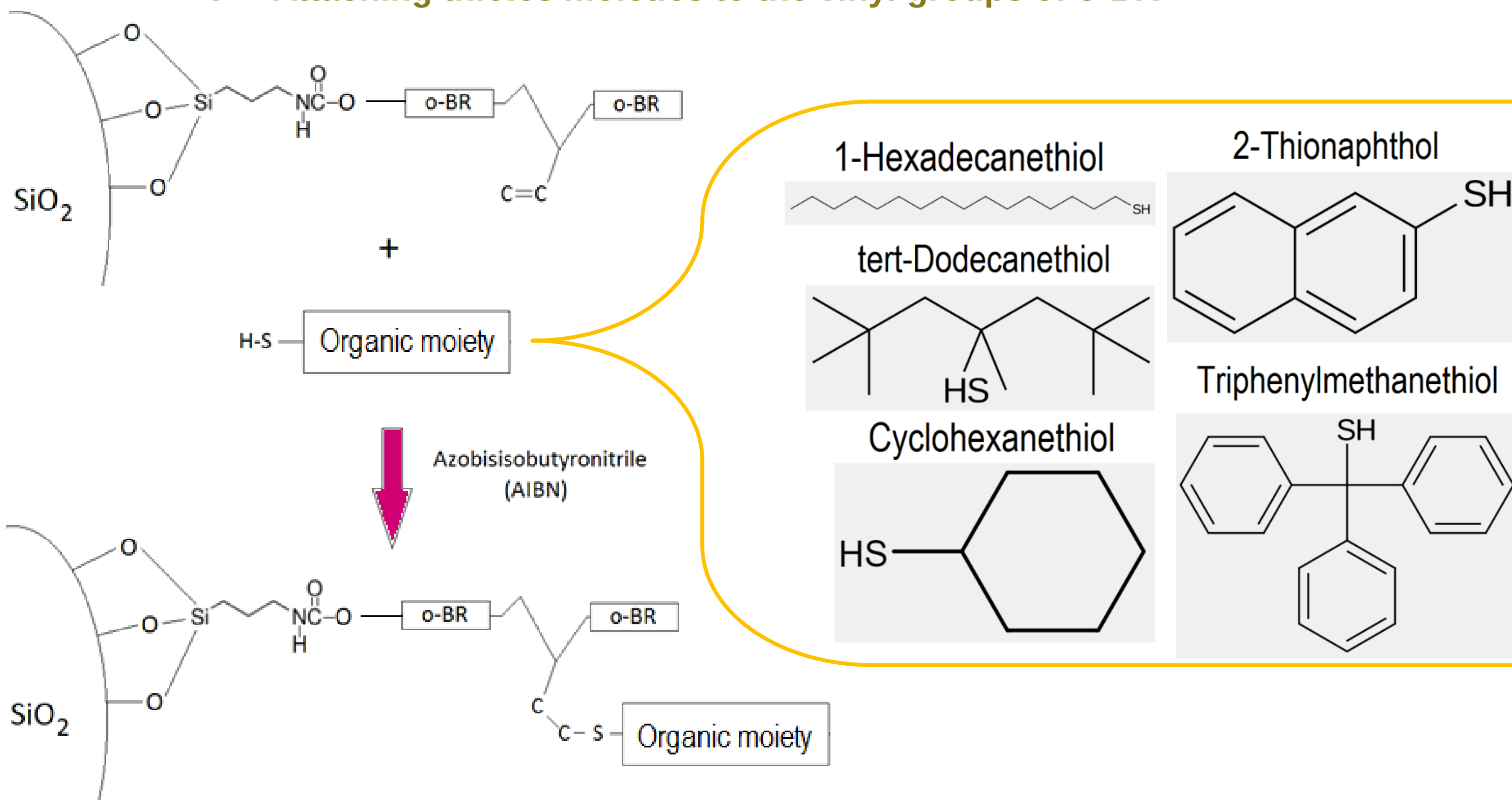
3 - Additional treatment with trimethylethoxysilane in order to cover residual, reactive silanol groups



PROGRESS OF THE MODIFICATION

SCHEME OF SILICA-SURFACE MODIFICATION

4 – Attaching thioles moieties to the vinyl groups of o-BR



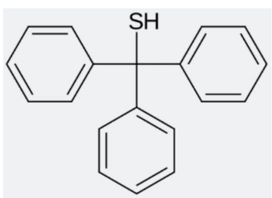
BRANCHING OF OLIGOMER-BACKBONE

TELECHELIC BUTADIENE OLIGOMER REACTIONS WITH THE THIOLES

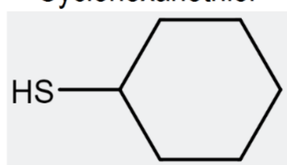
HO — o-BR
60 mers 1,2-vinyl

+

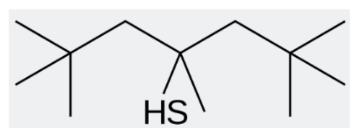
Triphenylmethanethiol



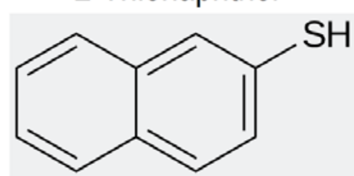
Cyclohexanethiol



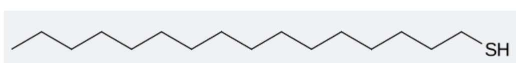
tert-Dodecanethiol



2-Thionaphthol



1-Hexadecanethiol

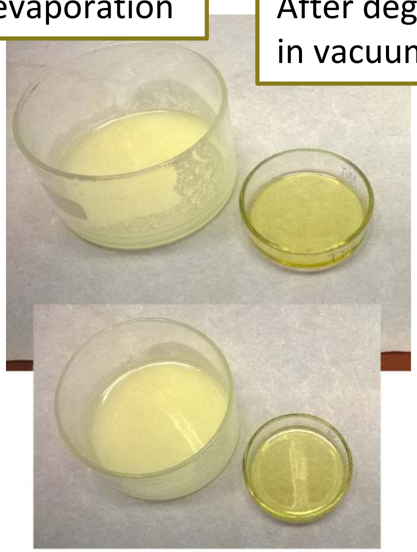


Procedure parameters:

Duration – 1 hour
Temperature – 65-70 °C (constant growth)
Mechanical stirring – 150 rpm
Atmosphere – nitrogen
Evaporation – 24 hours, 70 °C
Degassing - 24 hours, 70 °C (vacuum)

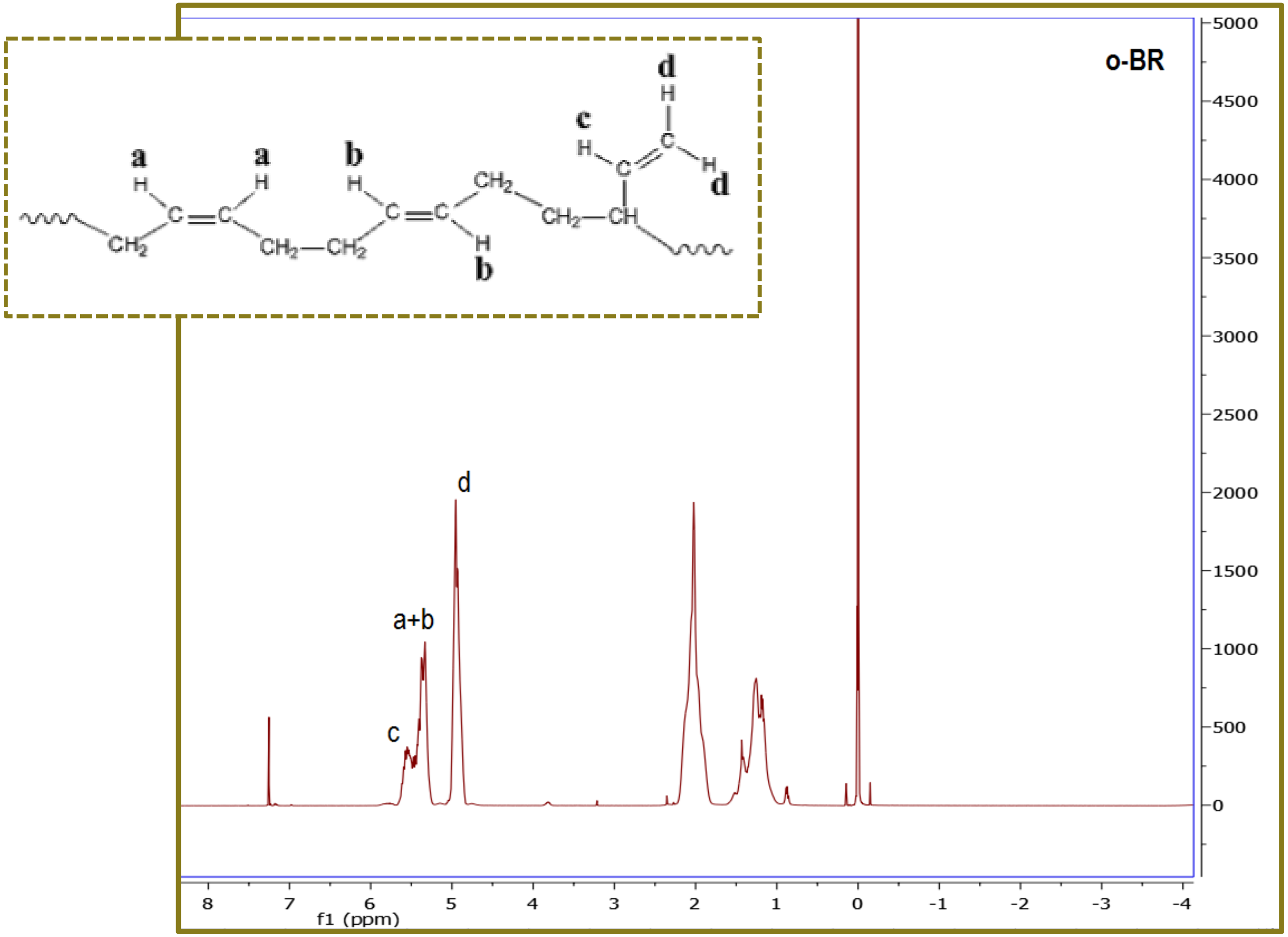
After evaporation

After degassing in vacuum oven



BRANCHING OF OLIGOMER-BACKBONE

OLIGOMER BRANCHING RESULTS ANALYSED BY **LS-NMR**



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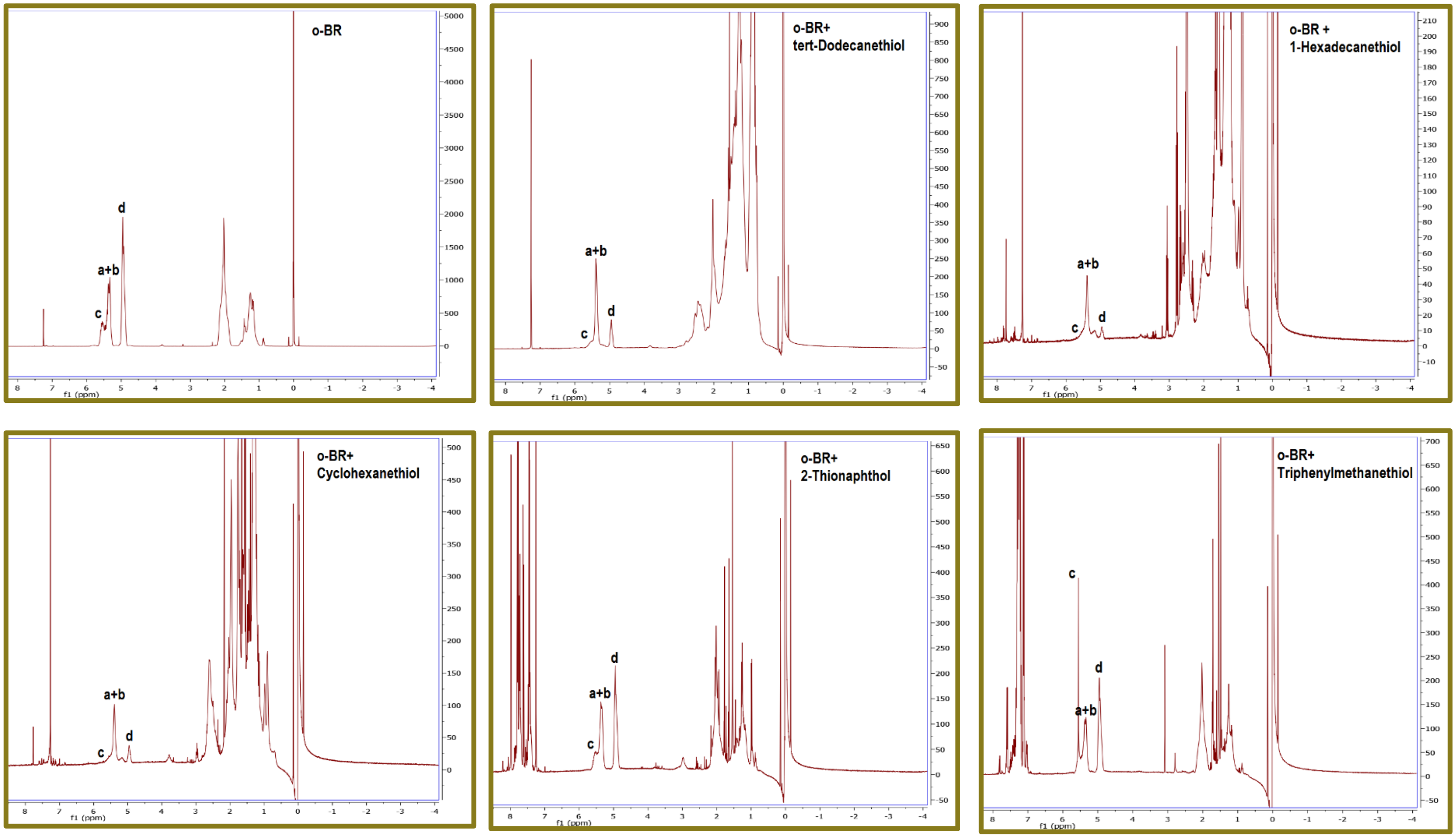
X. Liu, T. Zhou, Y. Liu, A. Zhang, C. Yuan & W. Zhang (2015) Cross-linking process of cis-polybutadiene rubber with peroxides studied by two-dimansional infrared correlation spectroscopy: a detailed tracking, *RSC Advances*, 5, 10231-10242, DOI: 10.1039/c4ra13502d

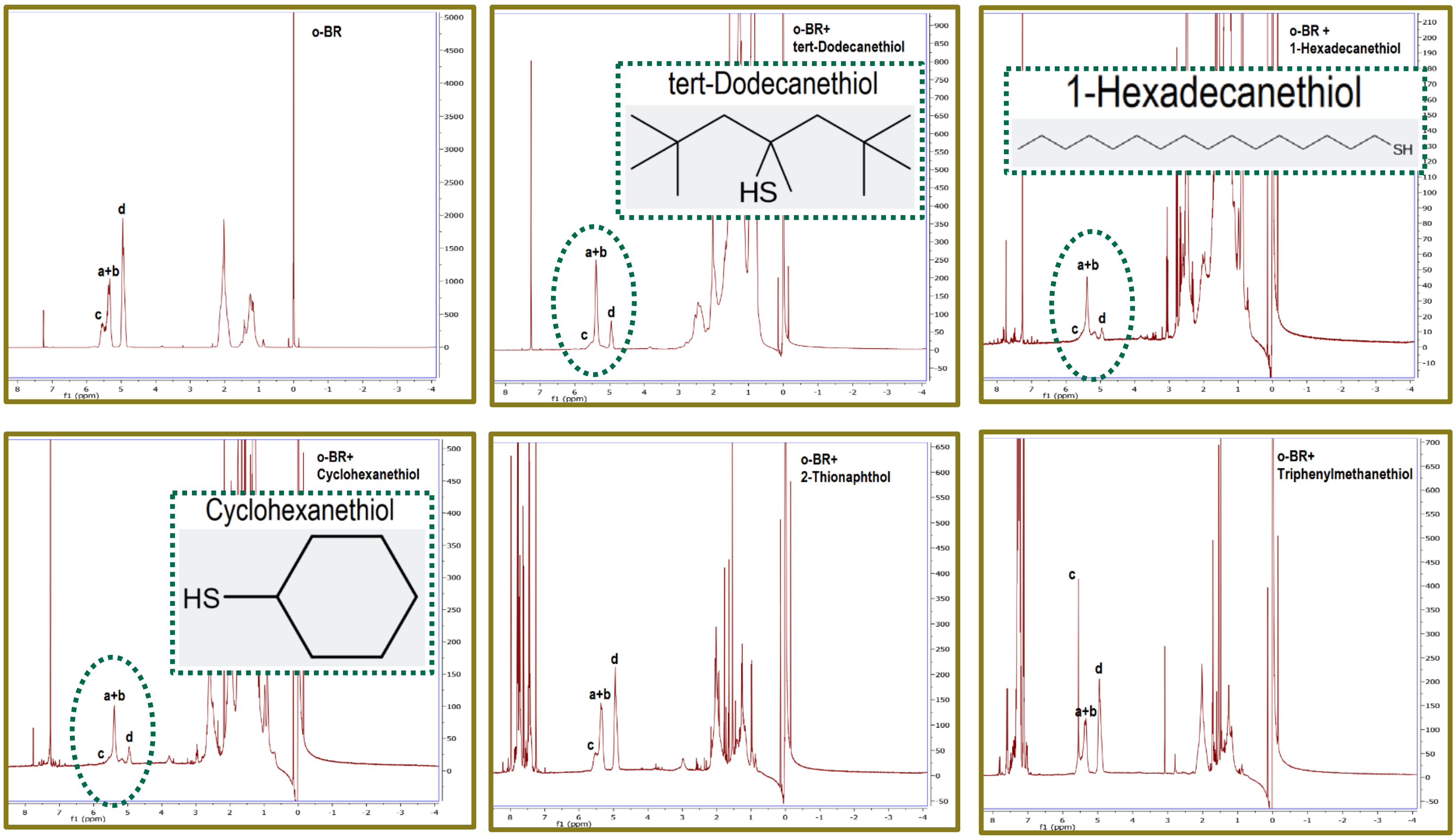
BRANCHING OF OLIGOMER-BACKBONE

OLIGOMER BRANCHING RESULTS ANALYSED BY **LS-NMR**



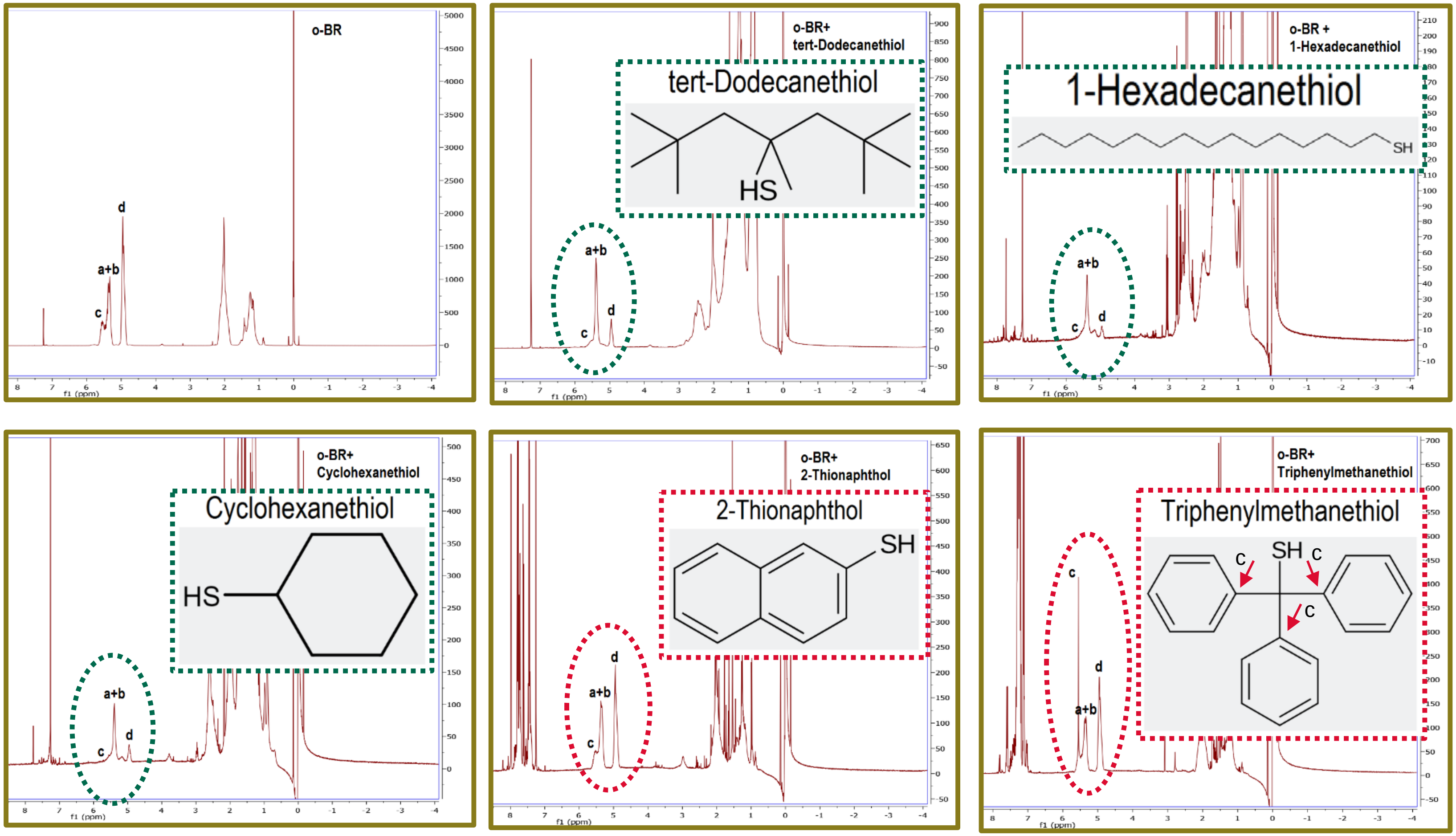
BRANCHING OF OLIGOMER-BACKBONE

OLIGOMER BRANCHING RESULTS ANALYSED BY LS-NMR



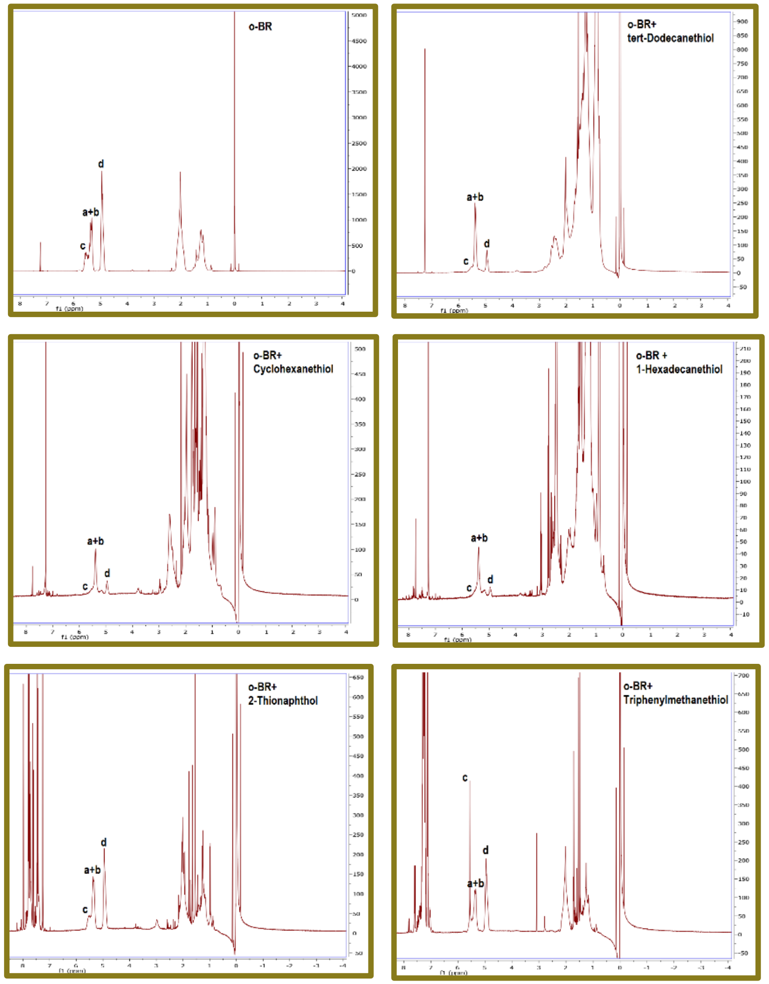
BRANCHING OF OLIGOMER-BACKBONE

OLIGOMER BRANCHING RESULTS ANALYSED BY LS-NMR



BRANCHING OF OLIGOMER-BACKBONE

OLIGOMER BRANCHING RESULTS ANALYSED BY **LS-NMR**



Presence of aromatic groups seems to influence negatively the effectiveness of the reaction.

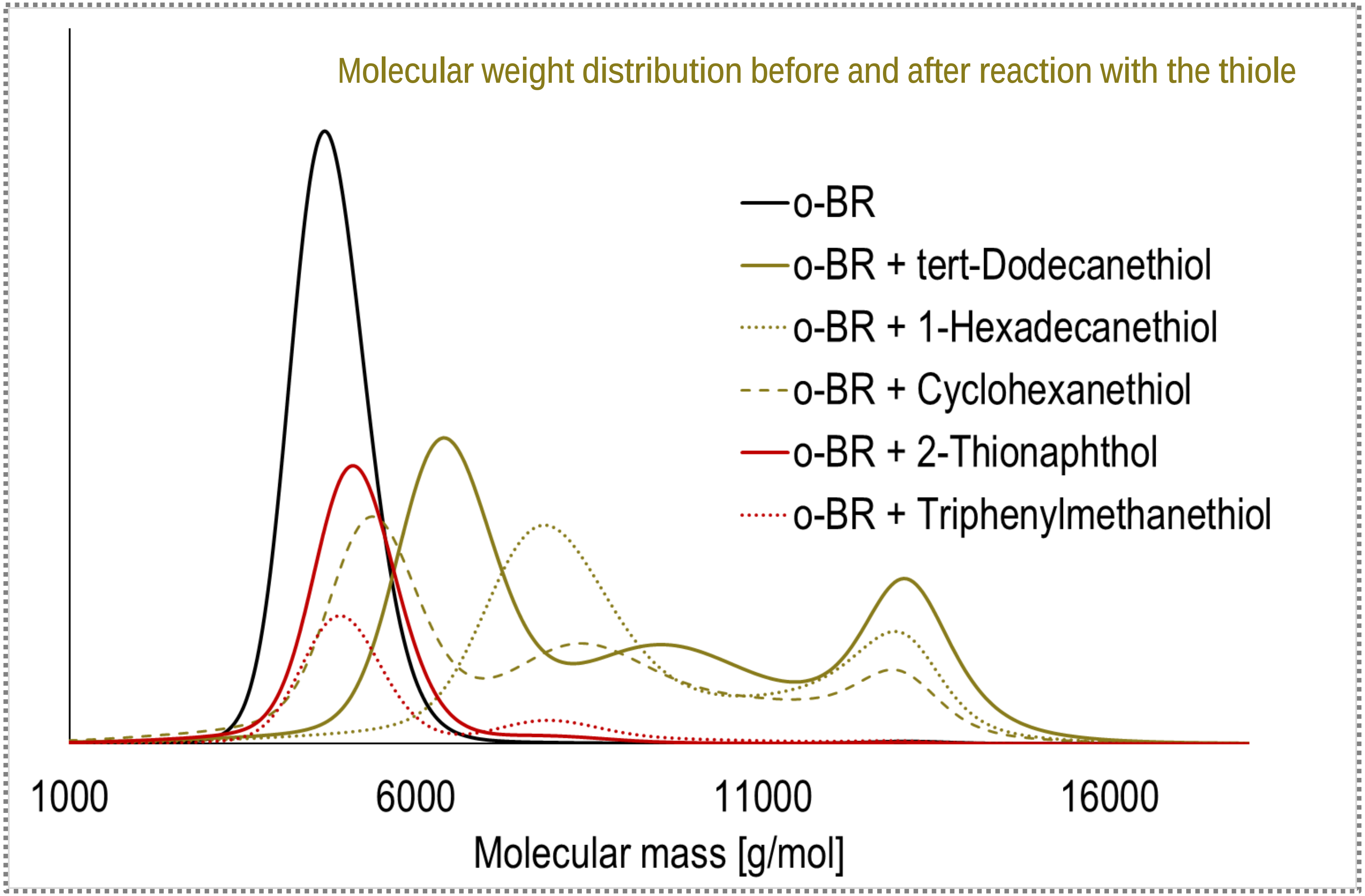
Sample	Integration ratio (d/a+b)
o-BR	1.351
o-BR + tert-Dodecanethiol	0.287
o-BR + Cyclohexanethiol	0.427
o-BR + 1-Hexadecanethiol	0.319
o-BR + 2-Thionaphthol	1.099
o-BR + Triphenylmethanethiol	1.316

Possibly presence of electron-donor alkyl group is necessary for effective grafting to vinyl groups.

Side reaction – **recombination** of thiole radicals?

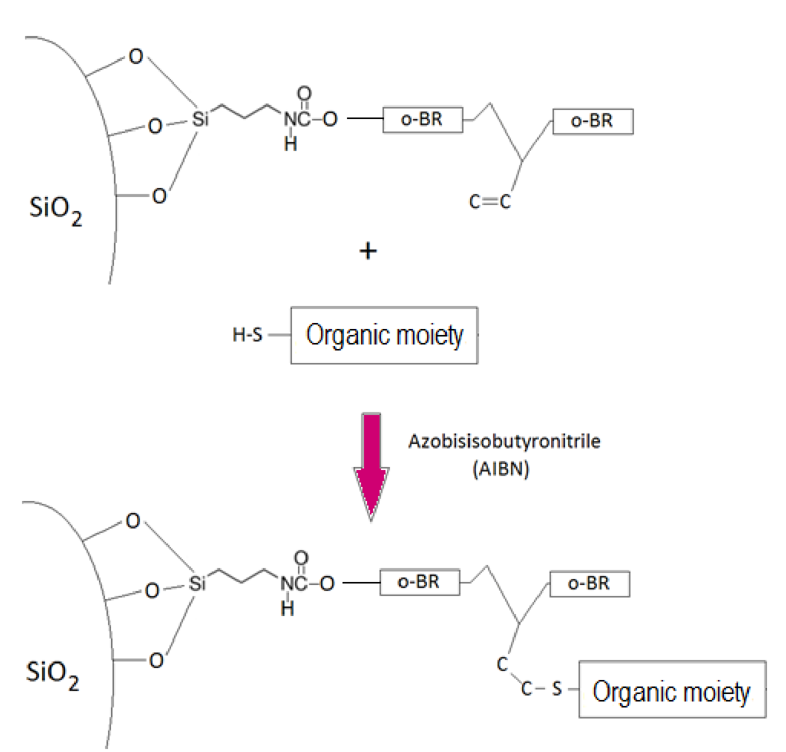
BRANCHING OF OLIGOMER-BACKBONE

OLIGOMER BRANCHING RESULTS ANALYSED BY GPC



BRANCHING OF OLIGOMER-BACKBONE

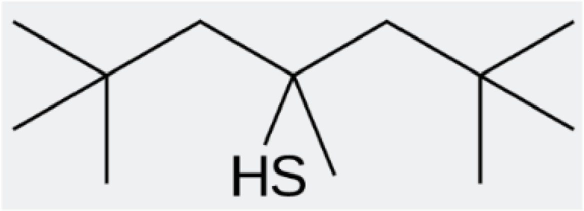
PROCEDURE CHARACTERISTICS



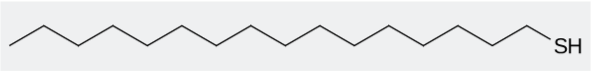
Procedure parameters:
Duration – 1 hour
Temperature – 65-70 °C (constant growth)
Mechanical stirring – 150 rpm
Atmosphere – nitrogen
Evaporation – 24 hours, 70 °C
Degassing - 24 hours, 70 °C (vacuum)

Thioles used for oligomer-backbone branching

tert-Dodecanethiol

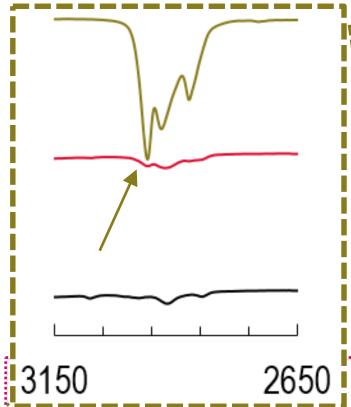


1-Hexadecanethiol

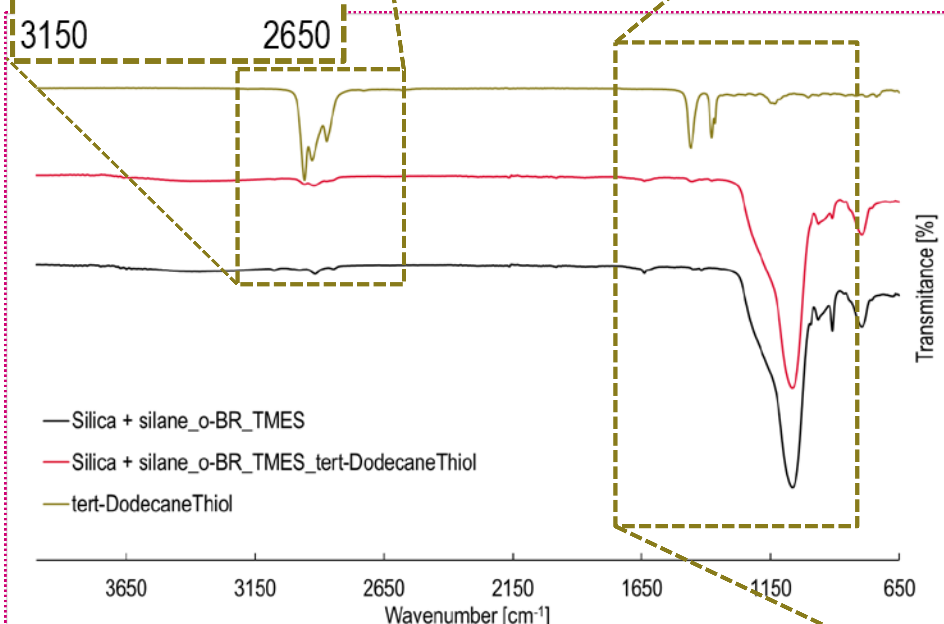


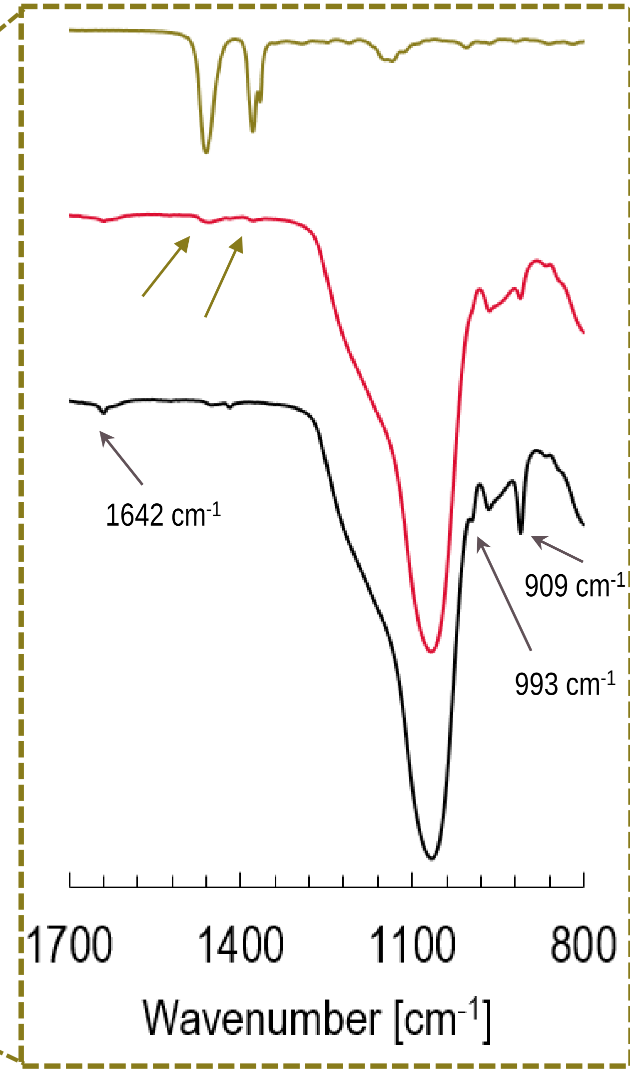
BRANCHING OF OLIGOMER-BACKBONE

GRAFTED-OLIGOMER BRANCHING ANALYSED BY FTIR



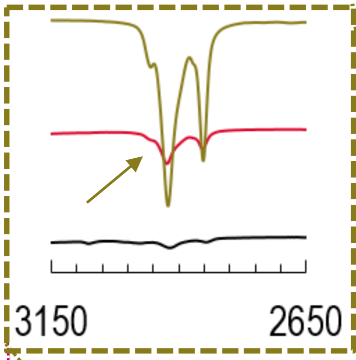
Sample	$Unsaturated_{i909}/Si\text{-}O\text{-}Si_{i1067}$
o-BR	0.296
o-BR + tert-Dodecanethiol	0.197



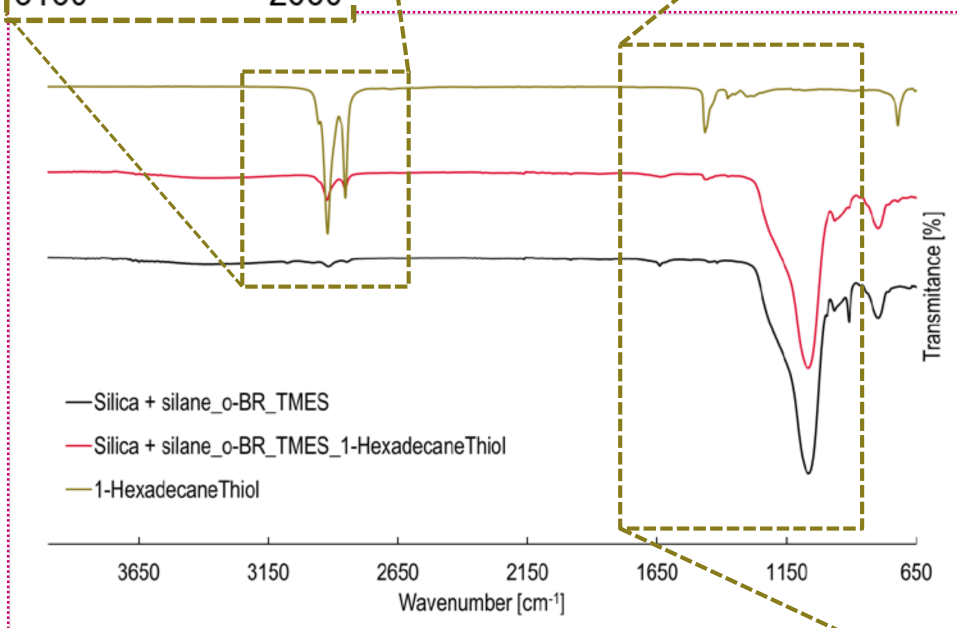


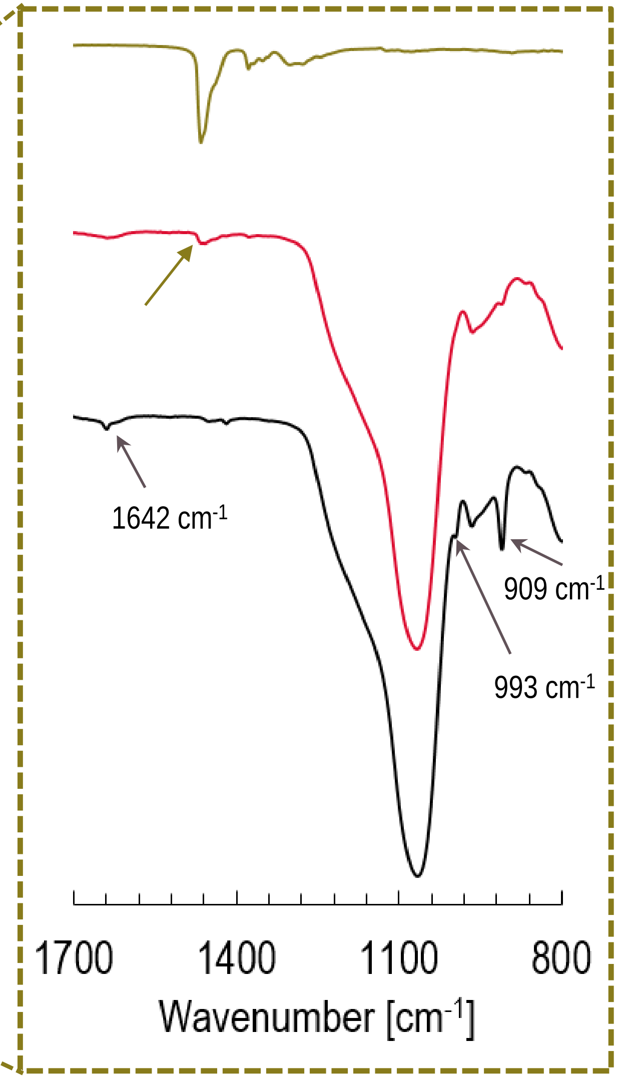
BRANCHING OF OLIGOMER-BACKBONE

GRAFTED-OLIGOMER BRANCHING ANALYSED BY FTIR



Sample	$Unsaturated_{i909}$/ $Si\text{-}O\text{-}Si_{i1067}$
o-BR	0.296
o-BR + 1-Hexadecanethiol	0.182



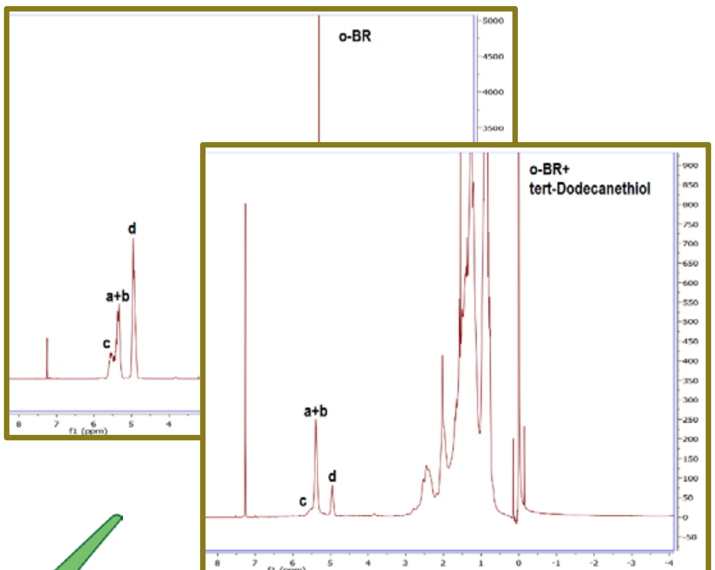


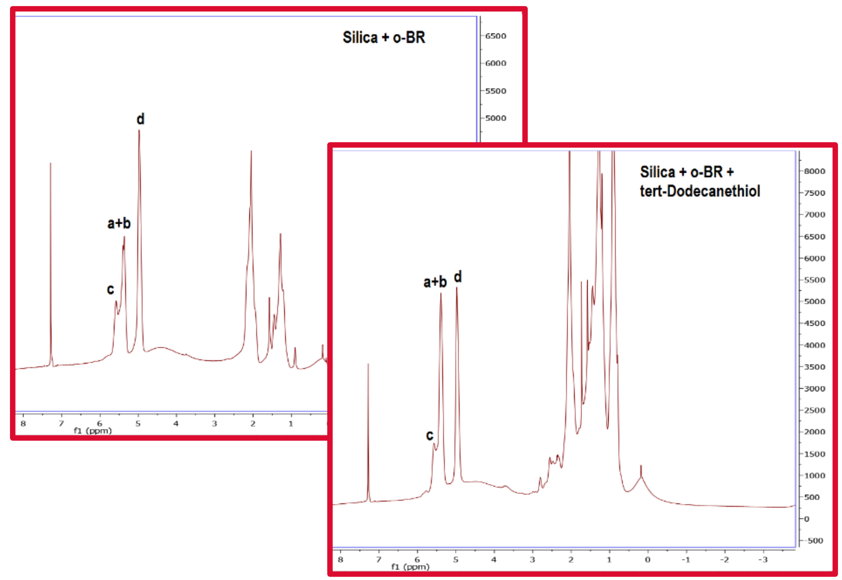
BRANCHING OF OLIGOMER-BACKBONE

GRAFTED VS NON-GRAFTED OLIGOMER BRANCHING ANALYSED BY HR-MAS NMR

Sample	Integration ratio (d/a+b)
o-BR	1.351
o-BR + tert-Dodecanethiol	0.287
% reacted vinyl groups	78.8 %

Sample	Integration ratio (d/a+b)
Silica + o-BR	1.235
Silica + o-BR + tert-Dodecanethiol	0.901
% reacted vinyl groups	27.0 %





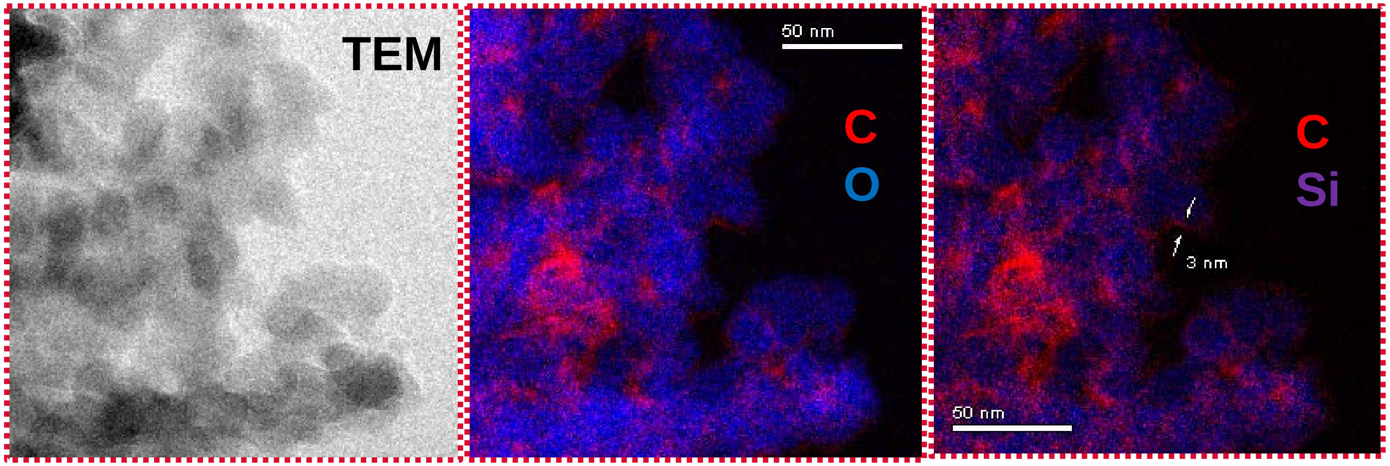
Negative influence of water?

Immobilization of thioles on silica surface?

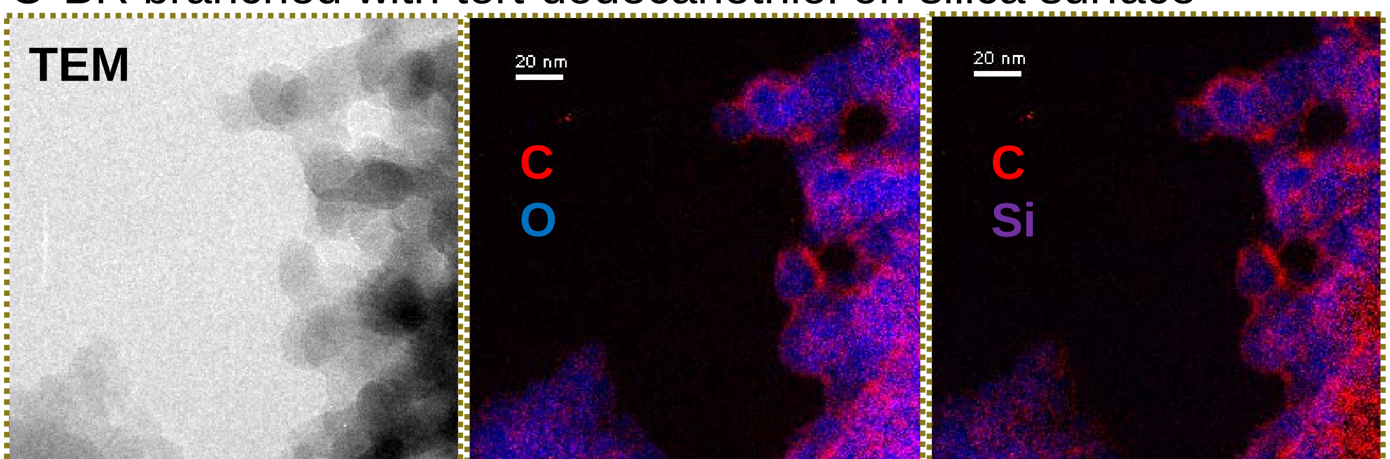
BRANCHING OF OLIGOMER-BACKBONE

BRANCHED VS NON-BRANCHED OLIGOMER ON SILICA ANALYSED BY EFTEM

Non-branched o-BR on silica surface



O-BR branched with tert-dodecanethiol on silica surface



GREEN MIXES PERFORMANCE

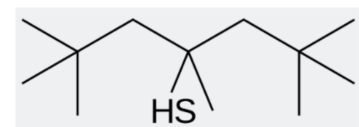
PREPARATION OF SILICA FILLED SSBR GREEN MIXES

SSBR 100 phr + 70 phr of:

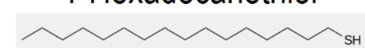
- Silica + Trimethylethoxysilane (TMES)
- Silica + Dodecyltriethoxysilane (D-DTES)
- Silica + Isocy_silane_o-BR + tert-Dodecanethiol
- Silica + Isocy_silane_o-BR + 1-Hexadecanethiol

Thioles

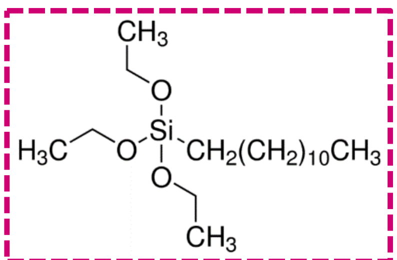
tert-Dodecanethiol



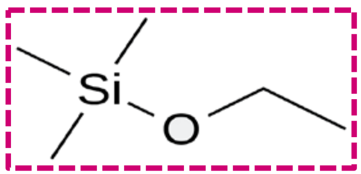
1-Hexadecanethiol



D-DTES



TMES

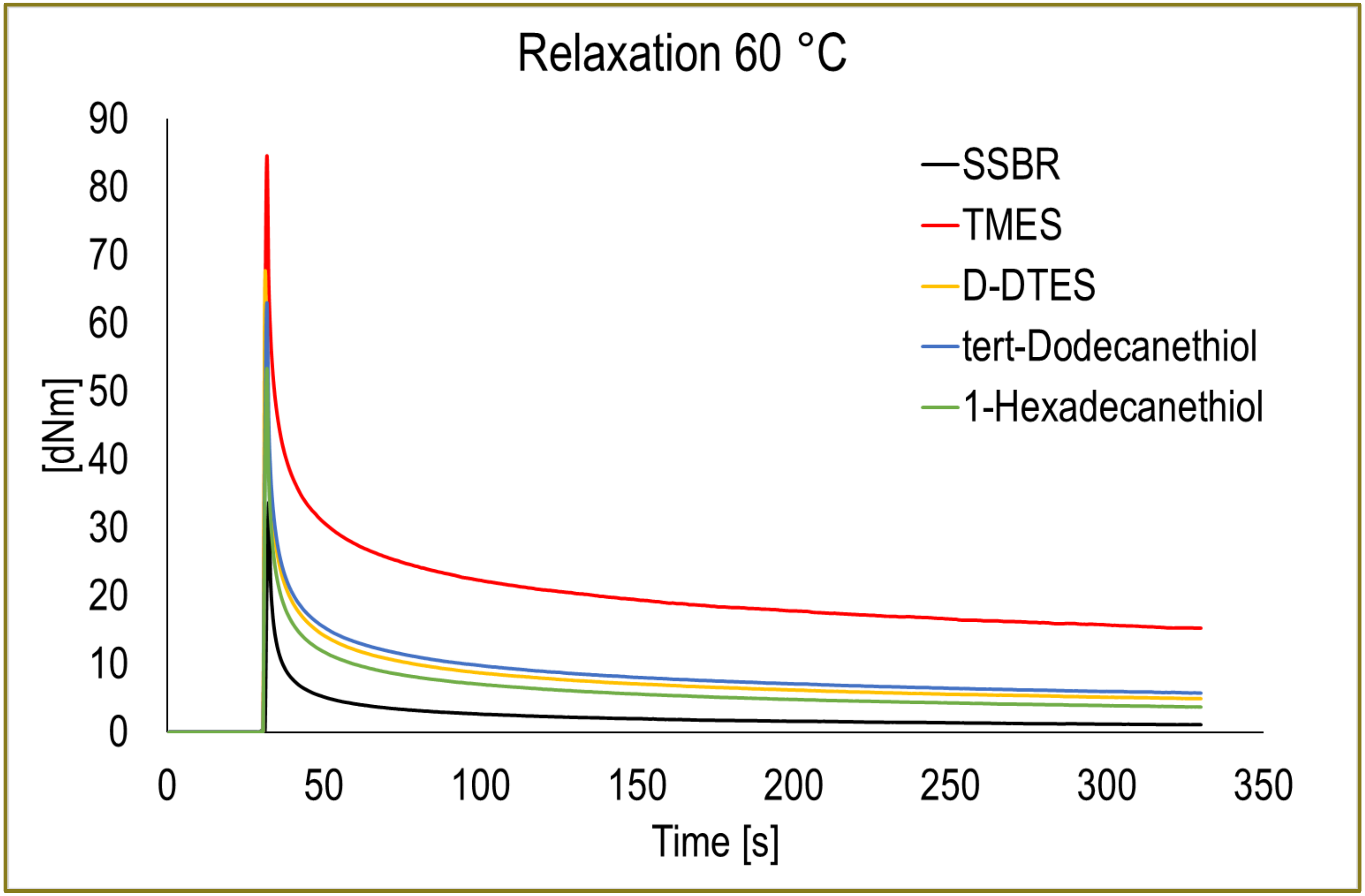


Mixing procedure

2 min	2 min	4 min
Introducing rubber	Introducing filler	Dispersion & homogenization

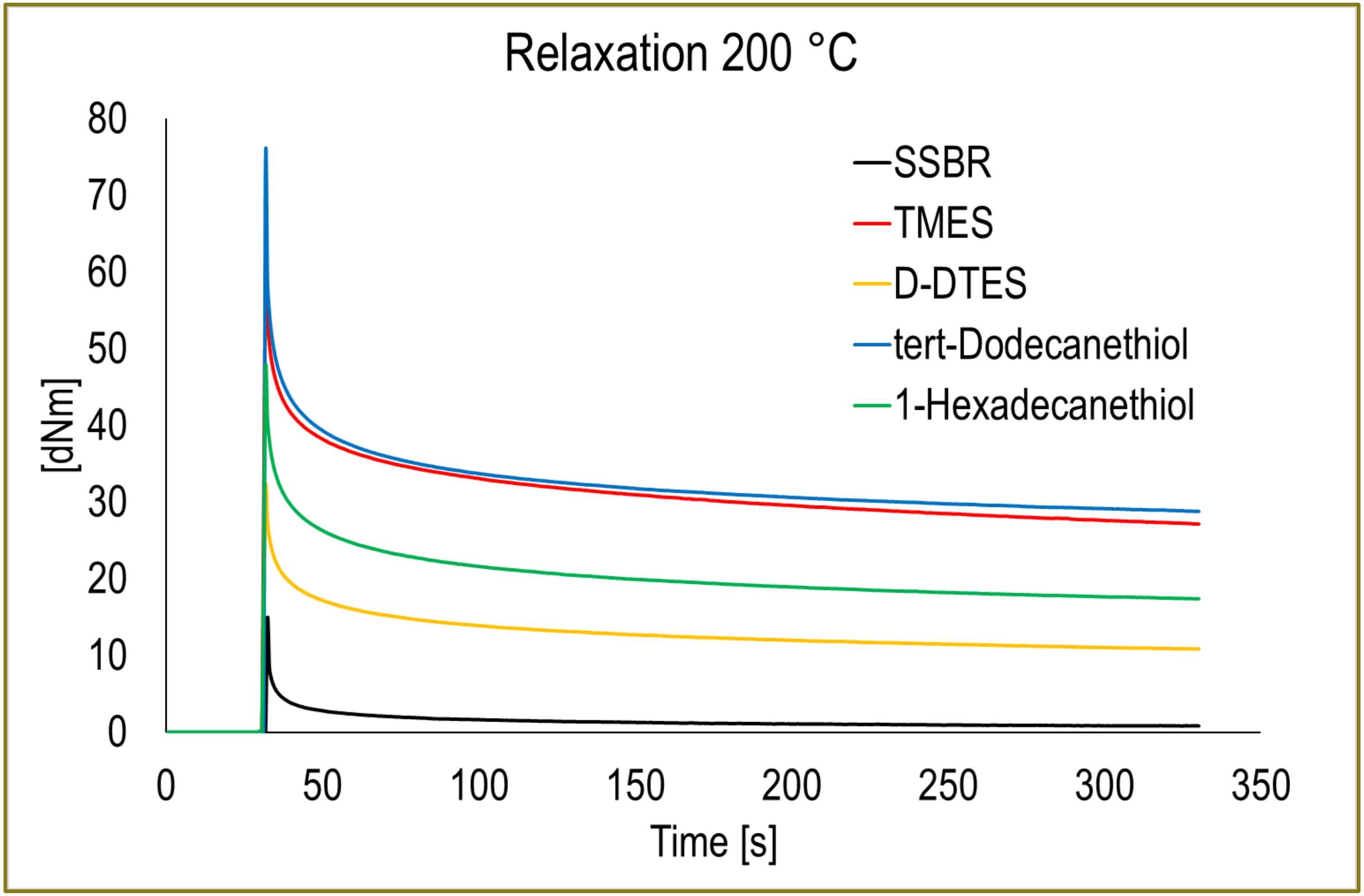
GREEN MIXES PERFORMANCE

PROPERTIES OF THE MIXES



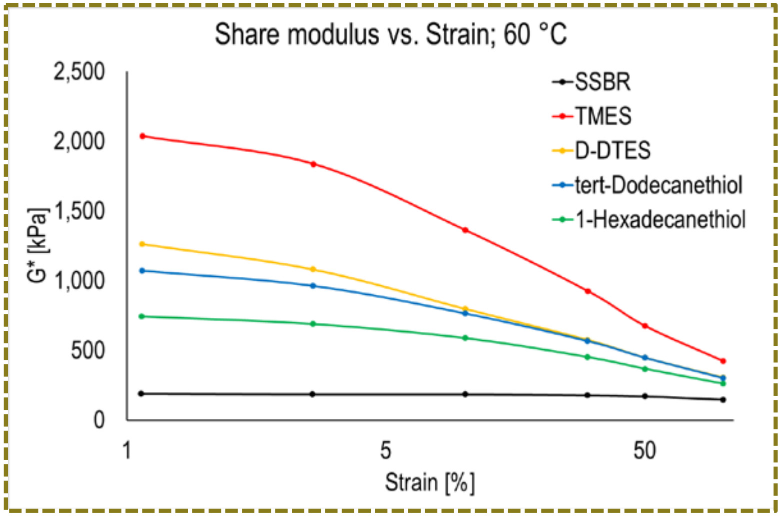
GREEN MIXES PERFORMANCE

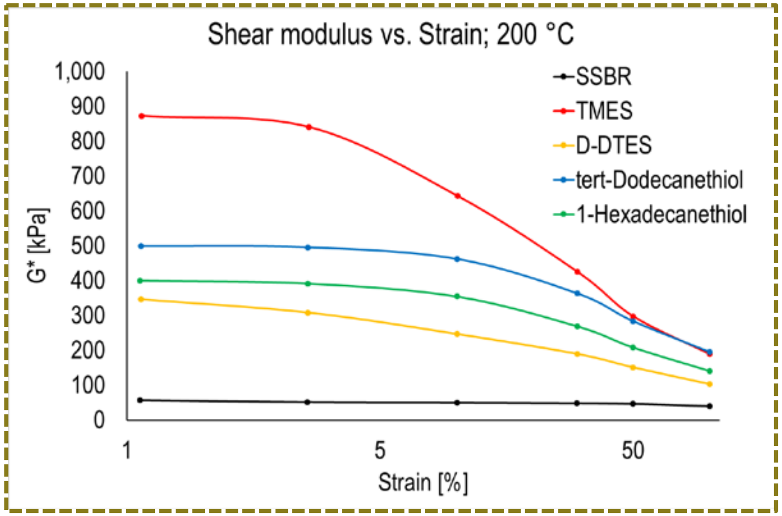
PROPERTIES OF THE MIXES

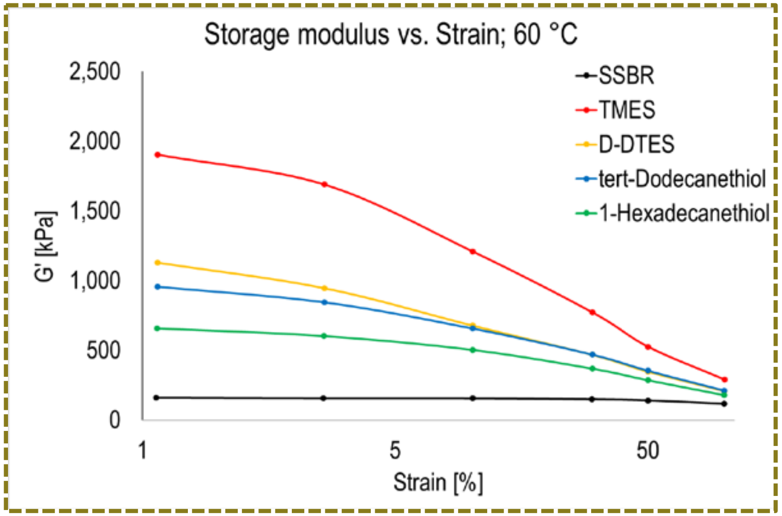


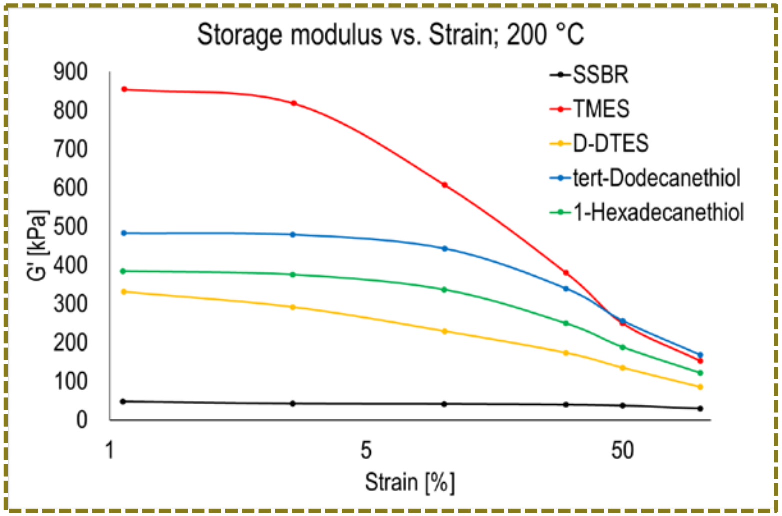
GREEN MIXES PERFORMANCE

PROPERTIES OF THE MIXES



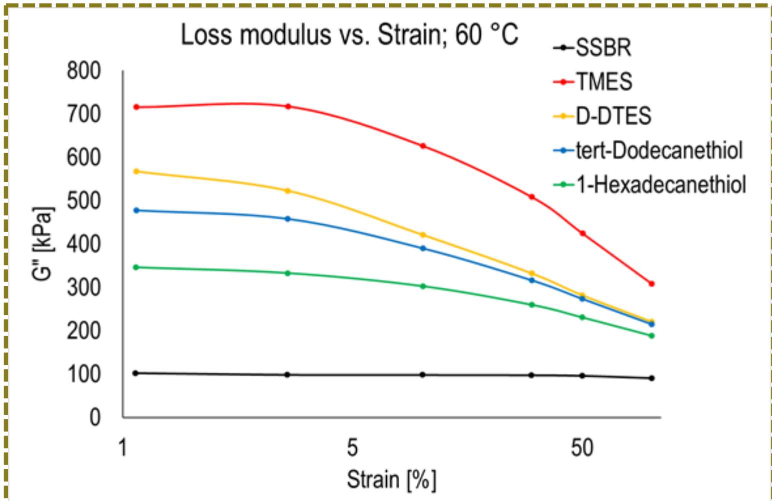


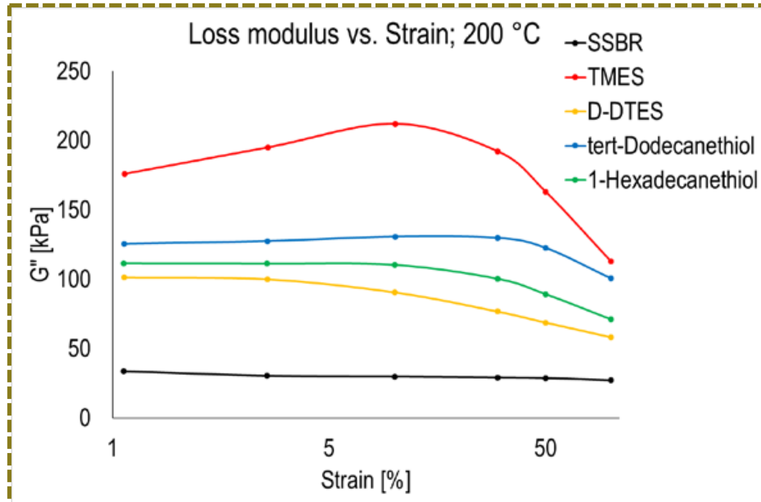


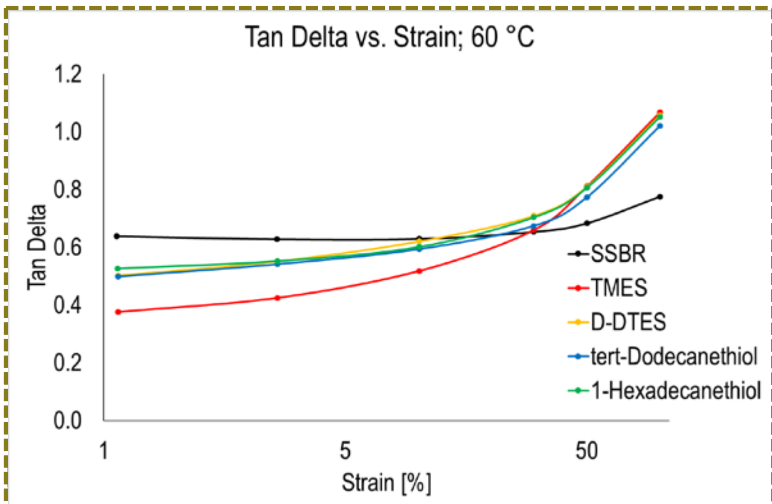


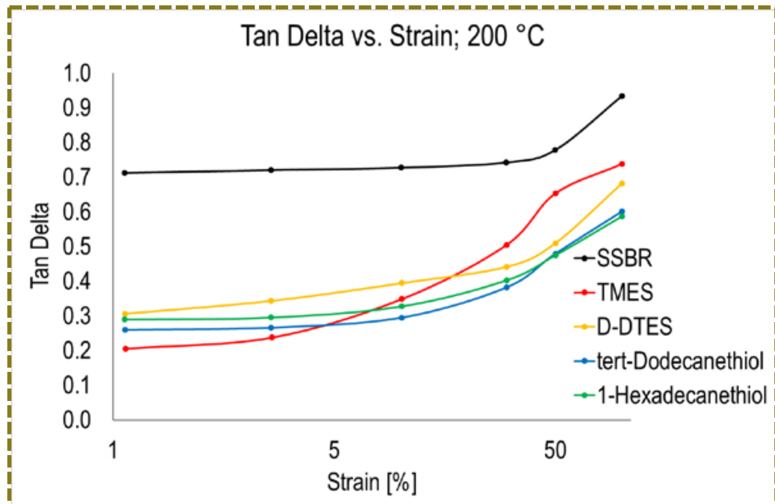
GREEN MIXES PERFORMANCE

PROPERTIES OF THE MIXES









SUMMARY
NEXT STEPS

O-BR modified with small-molecular thioles:

- TGA analysis of silica modified with the variuos compounds
- Enchancing efficiency and analysis of thioles reaction with vinyl groups of the oligomer backbone grafted and not-grafted on silica surface

Green mixes filled with the modified silica:

- Preparation of rubber samples filled with silica covered with o-BR and Cyclohexanethiol modified o-BR
- DMA analysis of the samples
- SEM and DisperGrader analysis of the samples

Conclusions:

- Reaction between telechelic monohydroxy-butadiene oligomer (o-BR) and isocyanate silane allows grafting of relatively large organic chains on silica surface with high efficiency.
- Utilization of polybutadiene backbone containing vinyl groups enables effective branching of the macromolecule with various thioles.
- Developed procedure provides a simple and effective method of long branched-molecules grafting on silica surface.
- Addition of modified silica to SSBR rubber results in interesting dynamic properties, especially at elevated temperature when macromolecular mobility is high.

UNIVERSITY OF TWENTE.

3 July 2018,
Nuremberg, Germany

Thank you for your kind attention!

DKT 2018
Deutsche Kautschuk-Tagung