Facile and sustainable functionalization method for preparing sp^2 carbon allotropes with different solubility parameters

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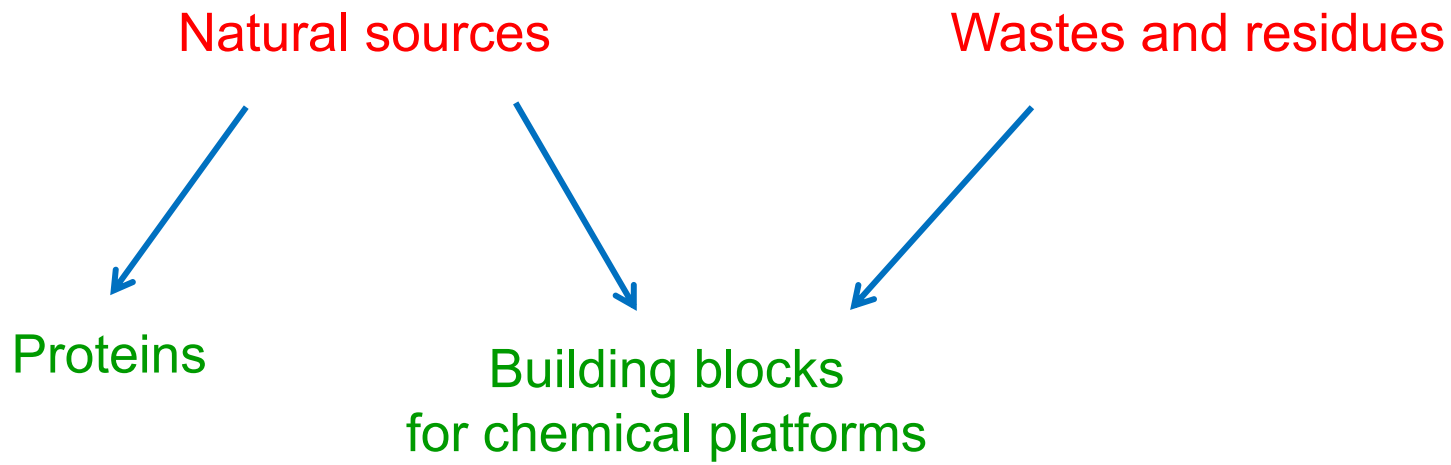
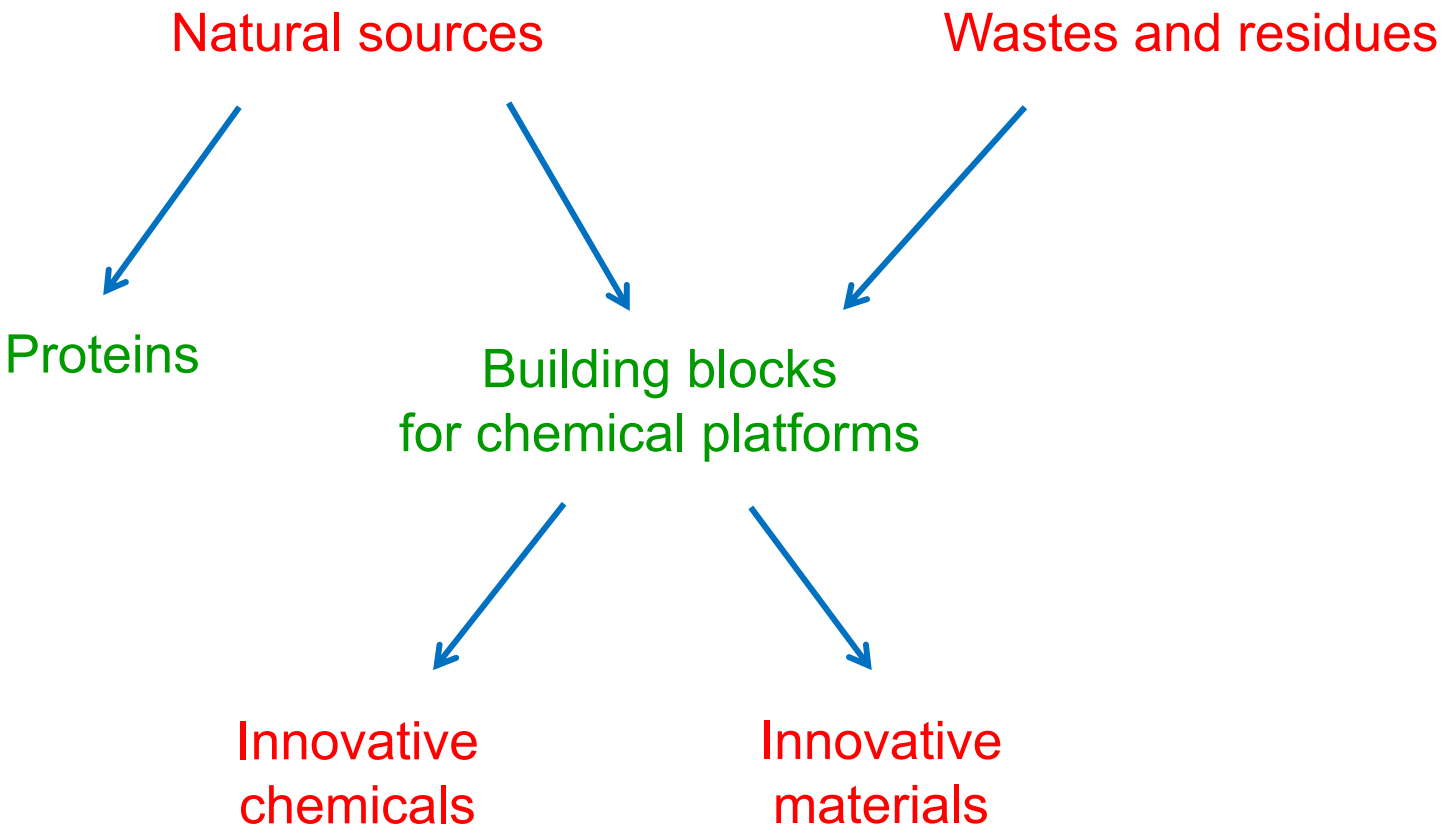
ISCaMaP

Innovative Sustainable Chemistry and Materials and Proteomics Group

Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering “G. Natta”


Natural sources
Wastes and residues
Proteins
Building blocks
for chemical platforms


Natural sources
Wastes and residues
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Building blocks
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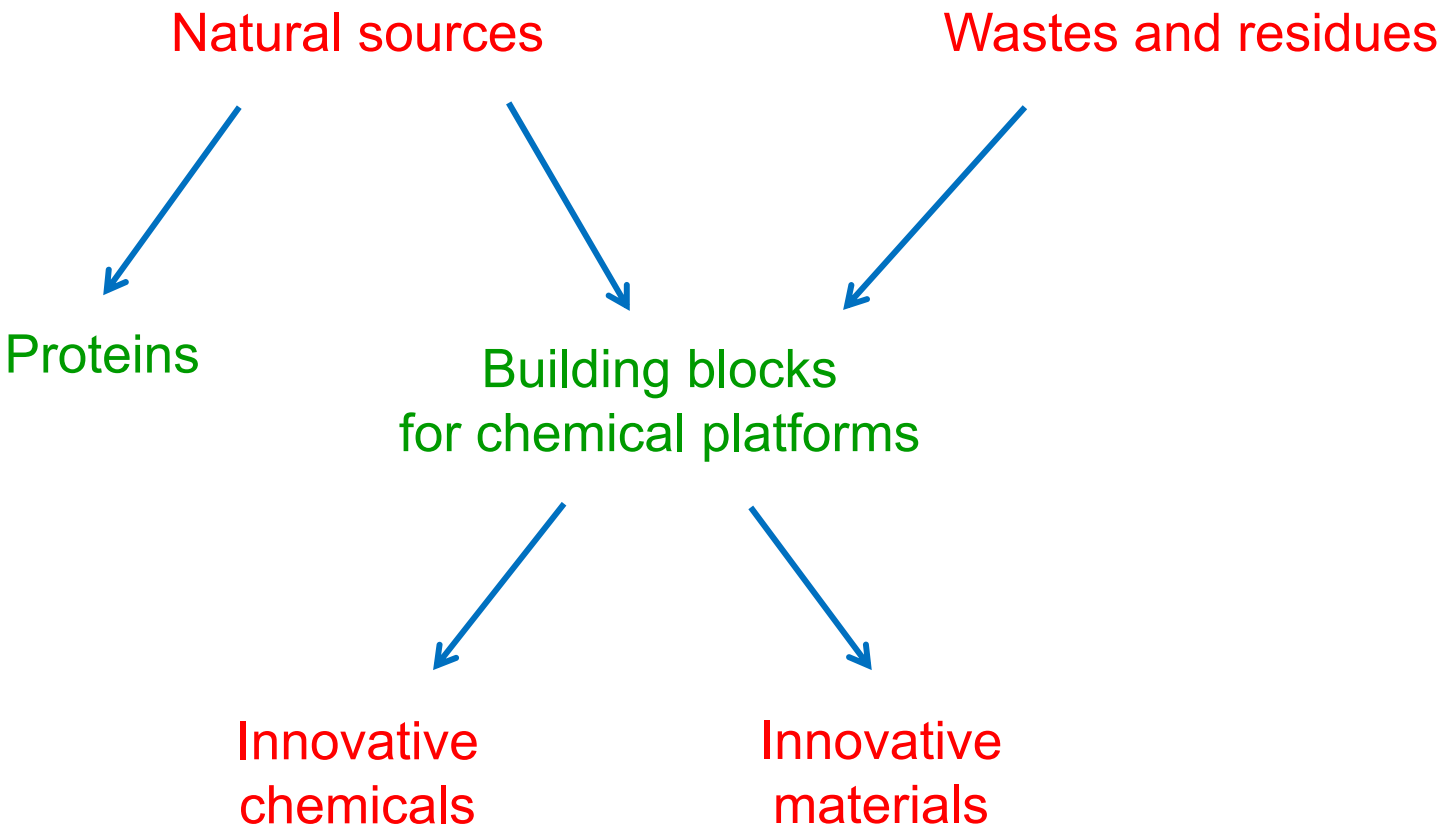
Innovative
chemicals
Innovative
materials



☞ Chemicals, Additives, Modifiers, Polymers

The DOE's Top Chemical Opportunities

Four Carbon 1,4-Diacids: Succinic, Fumaric and Malic

2,5-Furan dicarboxylic acid

3-Hydroxypropionic acid

Glucaric acid

Glycerol

Aspartic acid

Itaconic acid

3-Hydroxybutyrolactone

Sorbitol (Alcohol Sugar of Glucose)

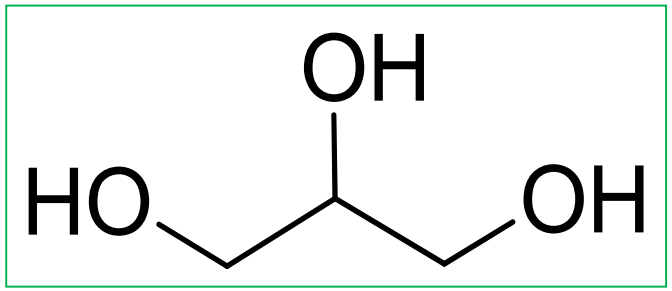
Xylitol/arabinitol (Sugar alcohols from xylose and arabinose)

Glutamic acid

Levulinic acid

DOE = US Department of Energy

Glycerol

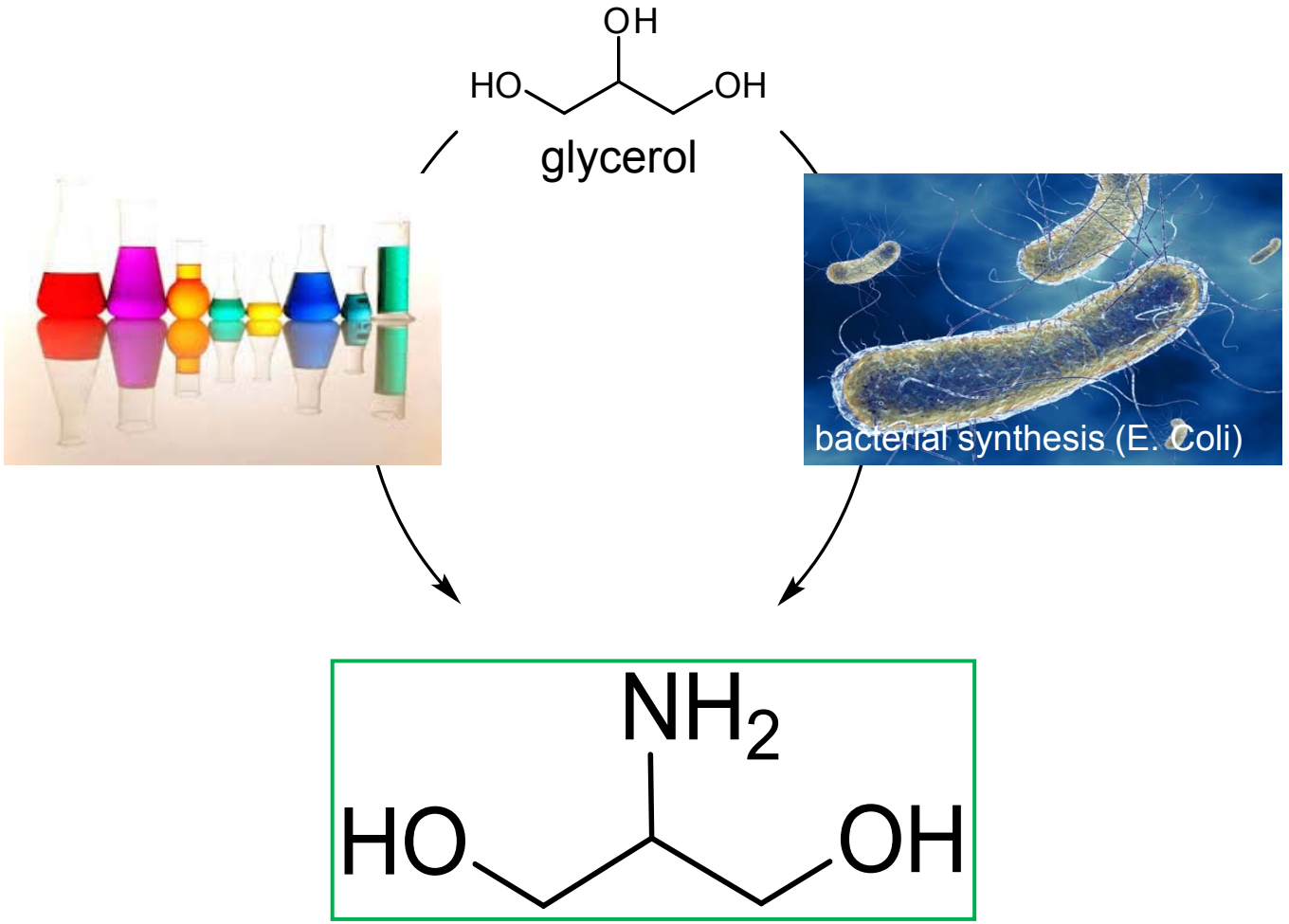


IUPAC: propane-1,2,3-triol
Formula: $C_3H_8O_3$
92.09 Da

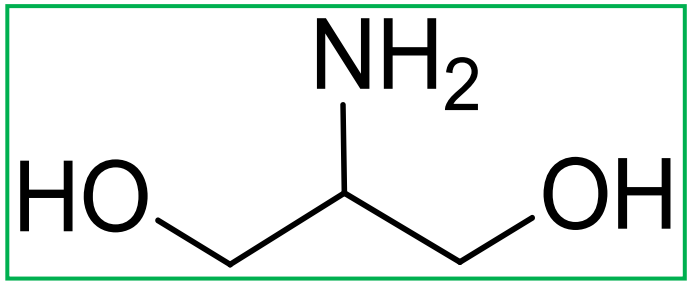
- ☞ easily available, cheap raw material
- ☞ main by-product of bio-diesel production
- ☞ not toxic
- ☞ biodegradable

M. Galimberti, V. Barbera, V. Cipolletti, S. Guerra, A. Citterio, Proceedings of Fall 186th Technical Meeting of the Rubber Division of the American Chemical Society, Inc. Nashville (TN) October 14 - 16, 2014

Selection of the building block: serinol

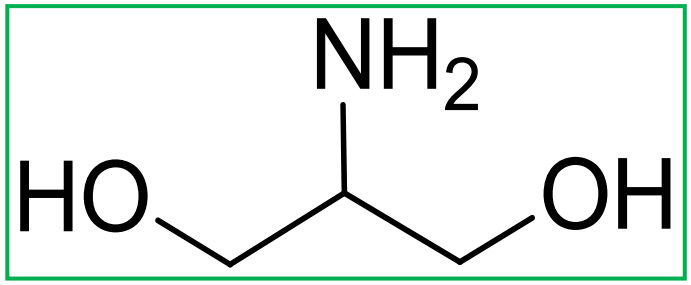


Selection of the building block: serinol



- Starting building block for many reaction pathways: many derivatives
- Chemoselectivity

Selection of the building block: serinol



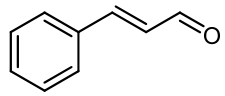
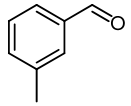
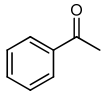
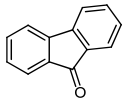
- Starting building block for many reaction pathways: many derivatives

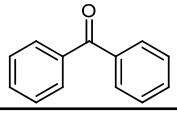
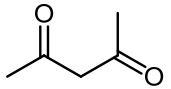
- Chemoselectivity

↓

Reactions of the amino group with carbonyl compounds

Reaction of serinol with carbonyl compounds

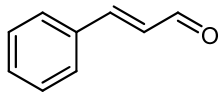
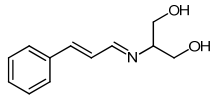
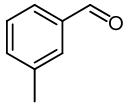
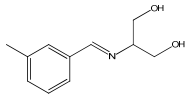
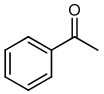
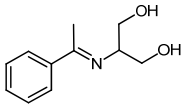
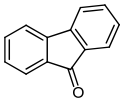
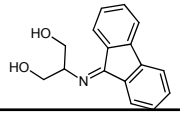
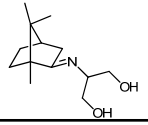
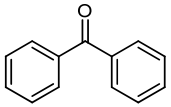
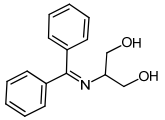
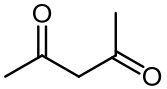
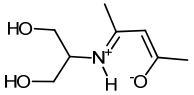
Carbonyl Compound





☞ Aromatic and sterically hindered carbonyl compounds

M. Galimberti, R. Sebastiano, V. Barbera, V. Cipolletti, G. Leonardi, S. Sun, L. Rossiello WO 2017/115253 A1

Imines from the Reaction of serinol with carbonyl compounds

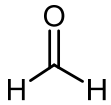
Carbonyl Compound	Product	Yield (%)
		92
		98
		83
		80
		70
		75
		95

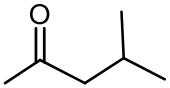
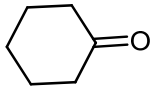
Imines

☞ Aromatic and sterically hindered carbonyl compounds lead to Imines

M. Galimberti, R. Sebastiano, V. Barbera, V. Cipolletti, G. Leonardi, S. Sun, L. Rossiello WO 2017/115253 A1

Reaction of serinol with carbonyl compounds

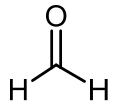
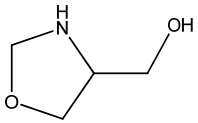
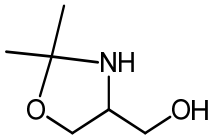
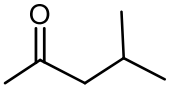
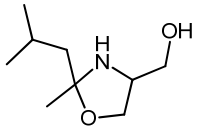
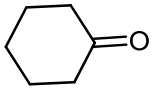
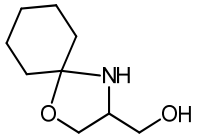
Carbonyl Compound


☞ Aliphatic carbonyl compounds with low steric hindrance

M. Galimberti, R. Sebastiano, V. Barbera, V. Cipolletti, G. Leonardi, S. Sun, L. Rossiello WO 2017/115253 A1

Oxazolidines from the Reaction of serinol with carbonyl compounds

Carbonyl Compound	Product	Yield (%)
		56
		90
		95
		90

Oxazolidines

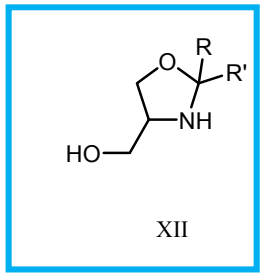
☞ Aliphatic carbonyl compounds with low steric hindrance lead to oxazolidines

M. Galimberti, R. Sebastiano, V. Barbera, V. Cipolletti, G. Leonardi, S. Sun, L. Rossiello WO 2017/115253 A1

Reaction of serinol with carbonyl compounds.

Without steric hindrance

and aromatic substituents

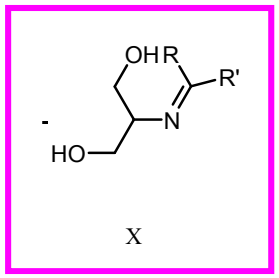


XII

Oxazolidines

With steric hindrance

and aromatic substituents



X

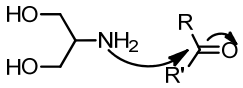
Imines

M. Galimberti, R. Sebastiano, V. Barbera, V. Cipolletti, G. Leonardi, S. Sun, L. Rossiello WO 2017/115253 A1

M. Galimberti, V. Barbera, S. Musto, G. Infortuna, V. Cipolletti, A. Citterio, S. Sun, Submitted to Rubber Chemistry and Technology, Frontiers Edition

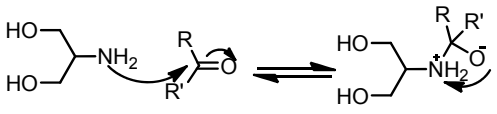
Reaction of serinol with carbonyl compounds – Hypothesis of a mechanism

The nucleophilic nitrogen reacts with carbonyl group



Reaction of serinol with carbonyl compounds – Hypothesis of a mechanism

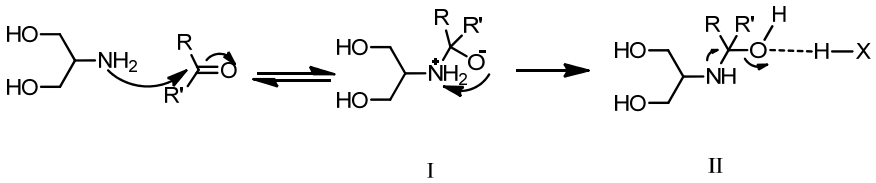
Proton transfer



I

Reaction of serinol with carbonyl compounds – Hypothesis of a mechanism

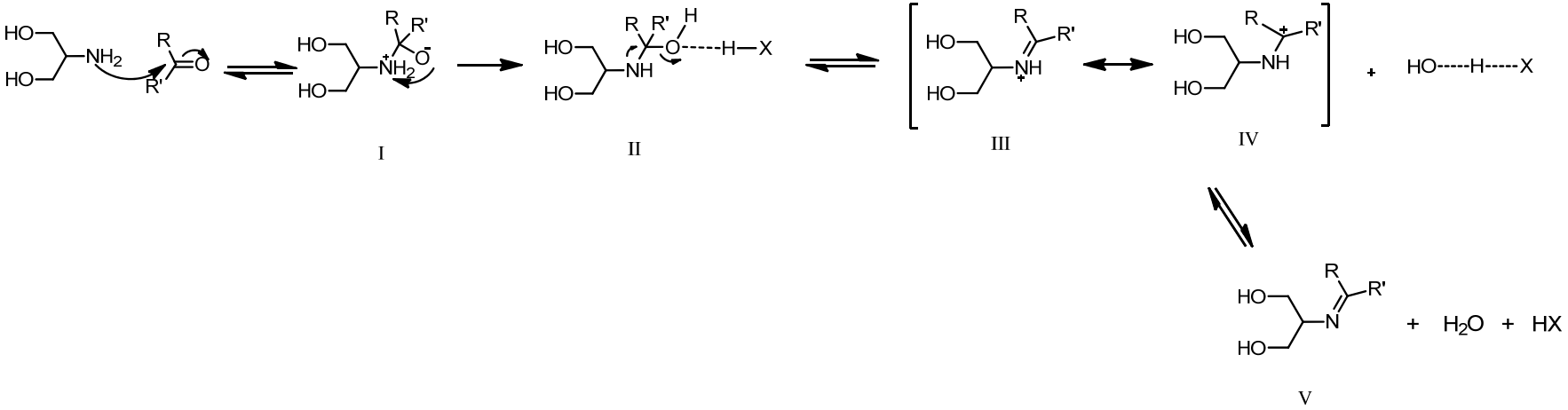
Release of a water molecule



I II

H—X = General or specific acid cat.

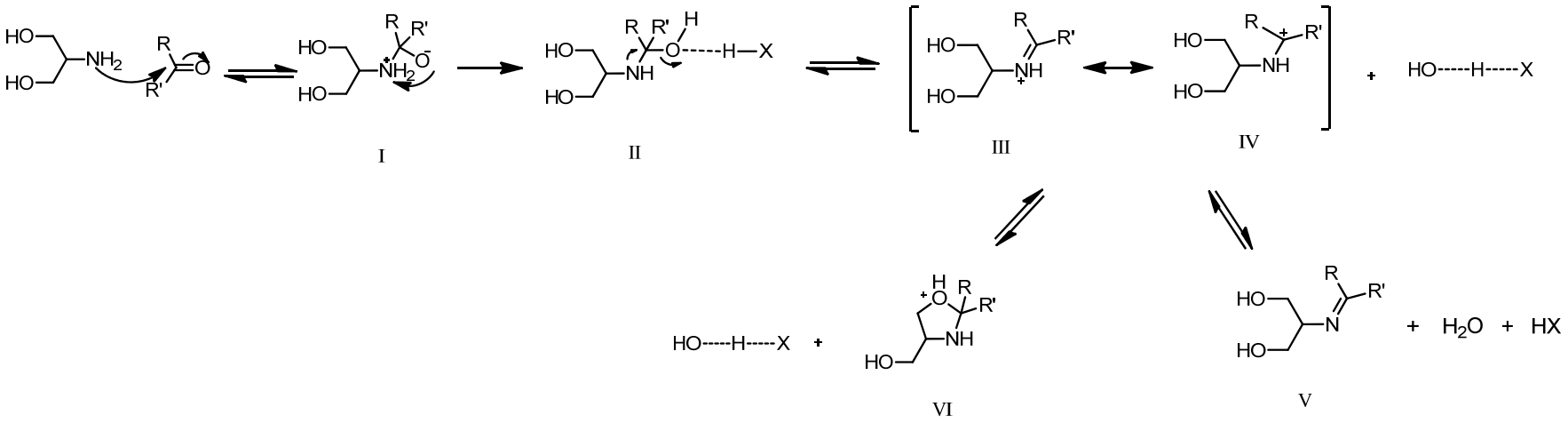
Reaction of serinol with carbonyl compounds – Hypothesis of a mechanism



Proton abstraction. Formation of an imine

H—X = General or specific acid cat.

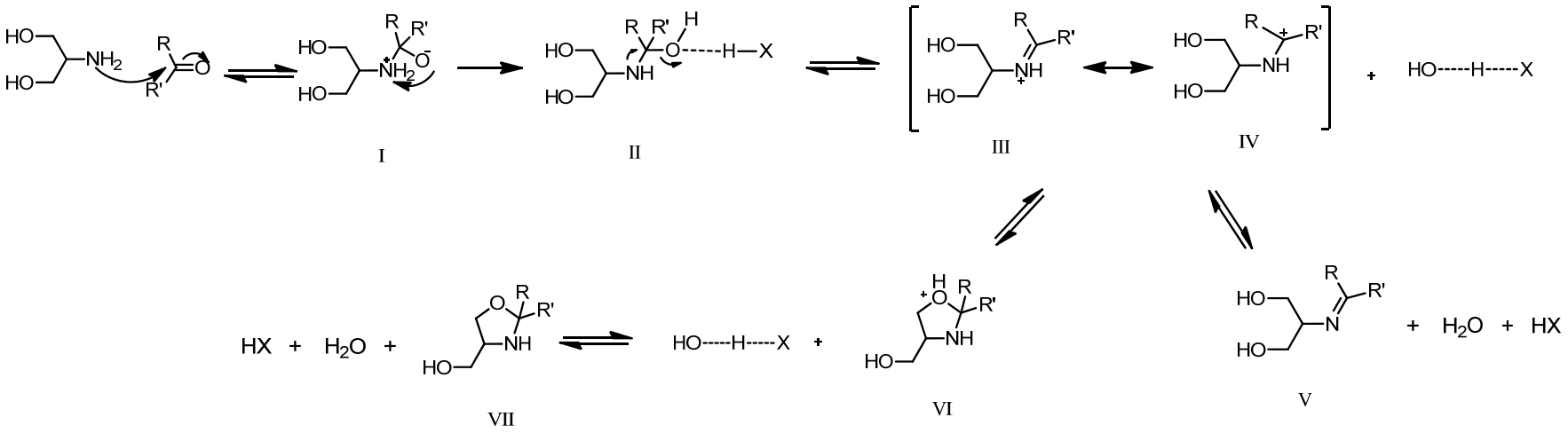
Reaction of serinol with carbonyl compounds – Hypothesis of a mechanism



Nucleophilic intramolecular addition: protonated oxazolidine

H—X = General or specific acid cat.

Reaction of serinol with carbonyl compounds – Hypothesis of a mechanism



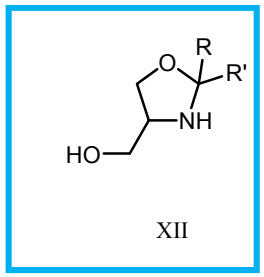
Proton abstraction

H—X = General or specific acid cat.

Reaction of serinol with carbonyl compounds.

Without steric hindrance

and aromatic substituents

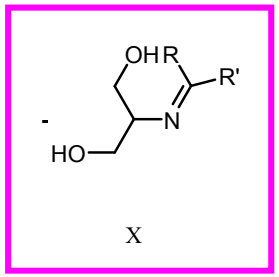


XII

Oxazolidines

With steric hindrance

and aromatic substituents



X

Imines

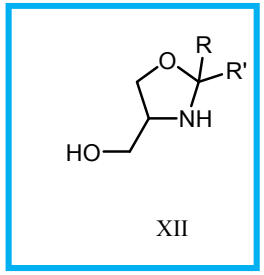
☞ Secondary accelerators for silica based compounds

M. Galimberti, V. Barbera, G. Infortuna, V. Cipolletti, A. Citterio, S. Sun Proceedings of International Elastomer Conference Cleveland (OH), October 9-12, 2017
M. Galimberti, V. Barbera, S. Musto, G. Infortuna, V. Cipolletti, A. Citterio, S. Sun, Submitted to Rubber Chemistry and Technology, Frontiers Edition

Reaction of serinol with carbonyl compounds.

Without steric hindrance

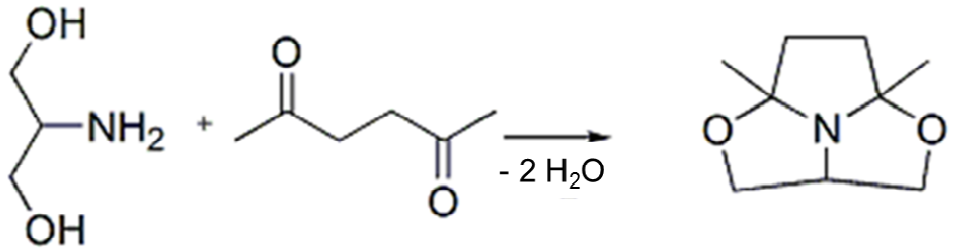
and aromatic substituents



XII

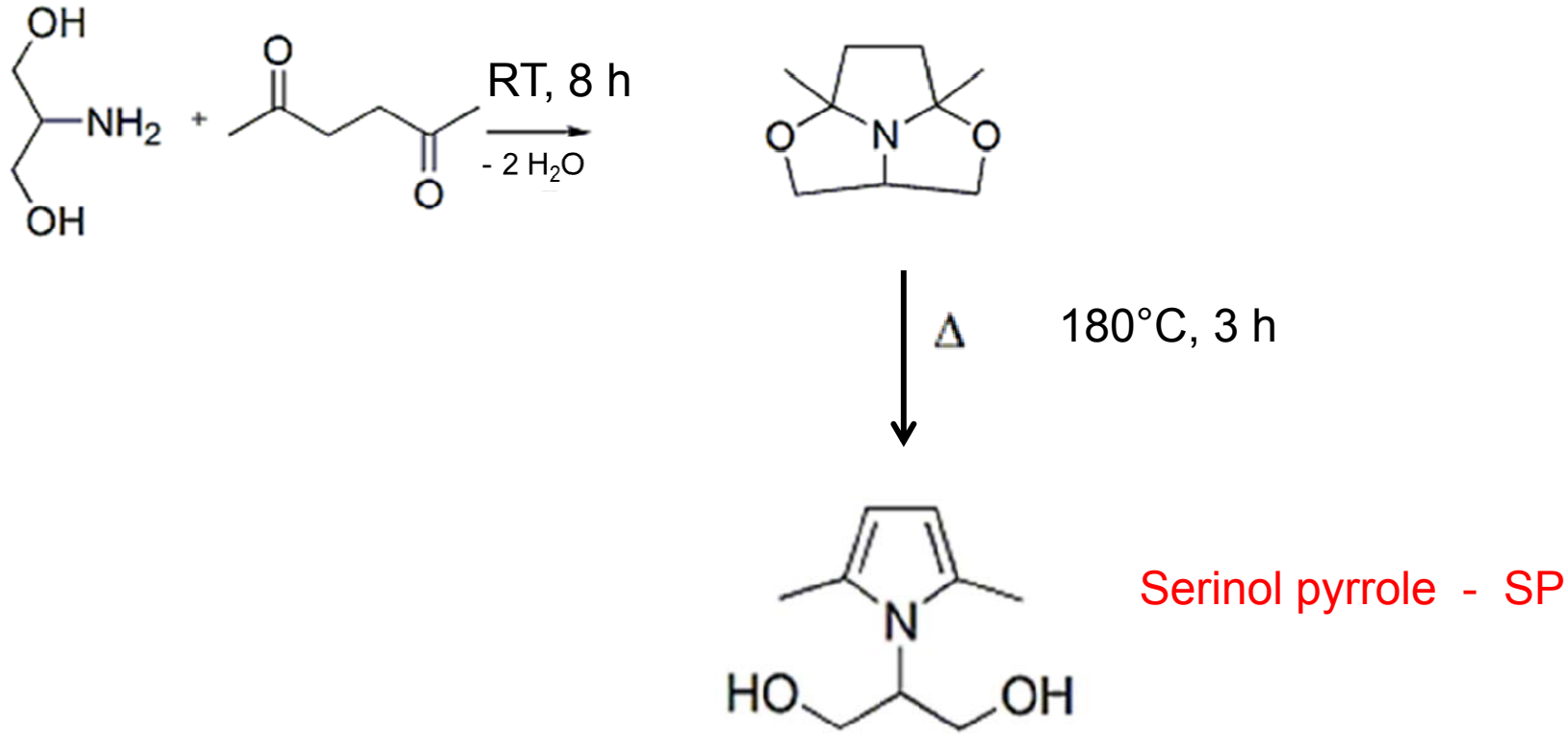
Oxazolidines

Reaction of serinol with dicarbonyl compound



V. Barbera, A.Citterio, M. Galimberti, G. Leonardi, R. Sebastiano, S.U.Shisodia, A.M. Valerio *WO 2015 189411 A1*
M. Galimberti, V. Barbera, A. Citterio, R. Sebastiano, A. Truscello, A. M. Valerio, L. Conzatti, R. Mendichi, *Polymer*, vol 63, 20 April 2015, Pages 62–70
M. Galimberti, V. Barbera, S. Guerra, L. Conzatti, C. Castiglioni, L. Brambilla, A. Serafini,, *RSC Adv.,* 2015, *5*, 81142-81152 DOI: 10.1039/C5RA11387C
V. Barbera, S. Musto, A. Citterio, L. Conzatti, M. Galimberti,, *eXPRESS Polymer Letters* 2016, *10* (7) 548–558

Reaction of serinol with dicarbonyl compound



Serinol pyrrole - SP

2-(2,5-dimethyl-1*H*-pirrol-1-yl) -1,3-propanediol

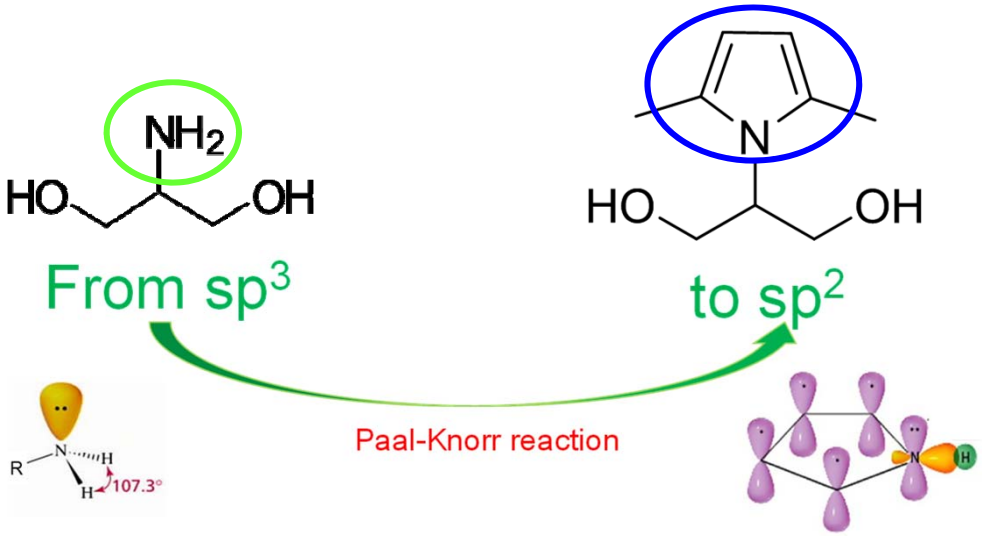
V. Barbera, A.Citterio, M. Galimberti, G. Leonardi, R. Sebastiano, S.U.Shisodia, A.M. Valerio *WO 2015 189411 A1*

M. Galimberti, V. Barbera, A. Citterio, R. Sebastiano, A. Truscello, A. M. Valerio, L. Conzatti, R. Mendichi, *Polymer*, vol 63, 20 April 2015, Pages 62–70

M. Galimberti, V. Barbera, S. Guerra, L. Conzatti, C. Castiglioni, L. Brambilla, A. Serafini,, *RSC Adv.*, 2015, *5*, 81142-81152 DOI: 10.1039/C5RA11387C

V. Barbera, S. Musto, A. Citterio, L. Conzatti, M. Galimberti,, *eXPRESS Polymer Letters* 2016, *10* (7) 548–558

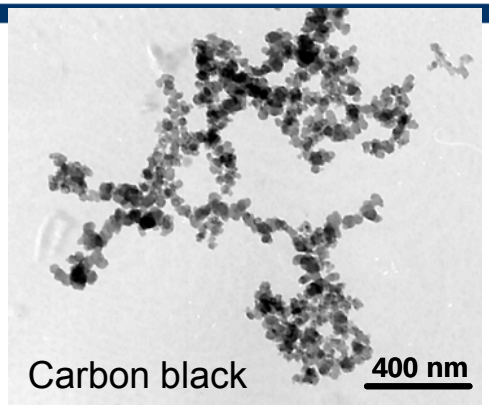
Neat synthesis of Serinol pyrrole

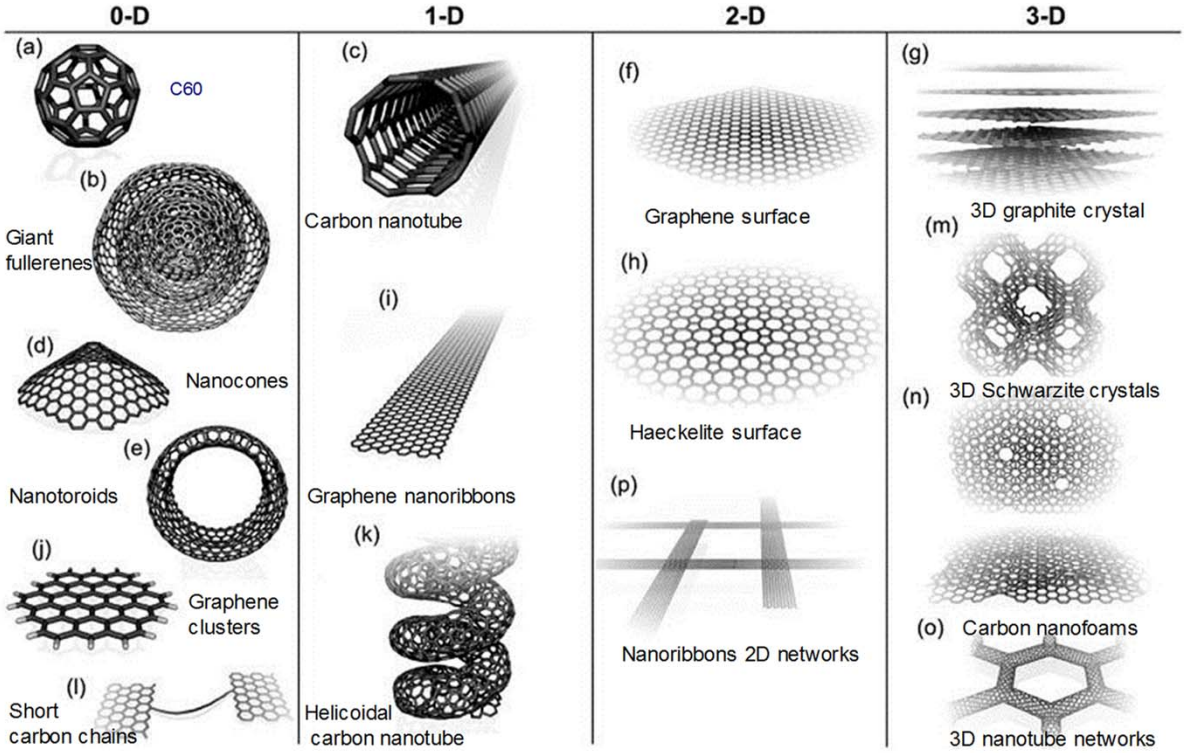


- Yield: at least 96%
- Atom efficiency: 85%
- Easy procedure
- No solvent
- By product: H_2O

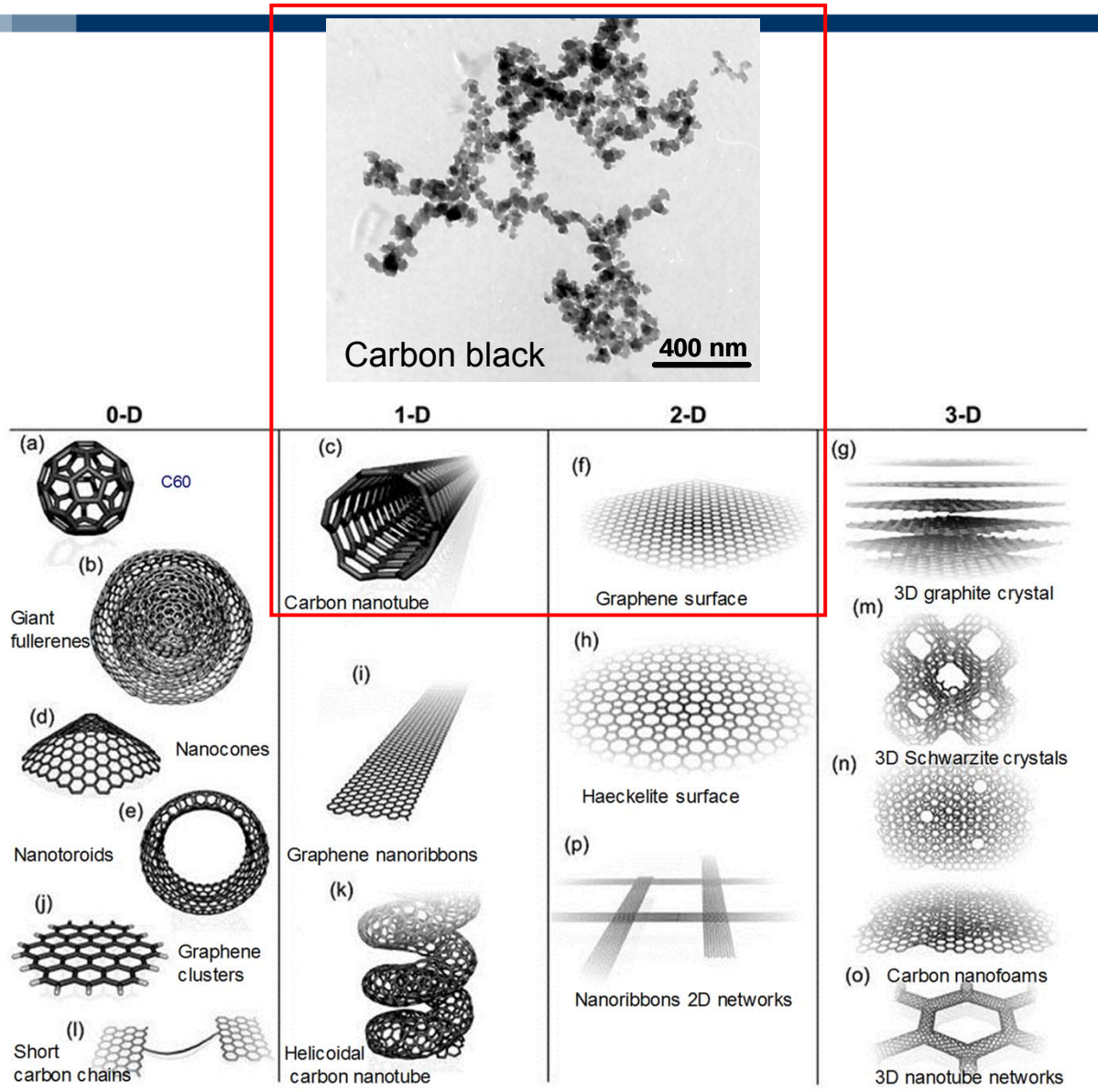
Functionalization of sp^2 carbon allotropes

sp^2 Carbon allotropes (CA)





sp^2 Carbon allotropes (CA)



CA-SP Adducts - Preparation

CA + SP

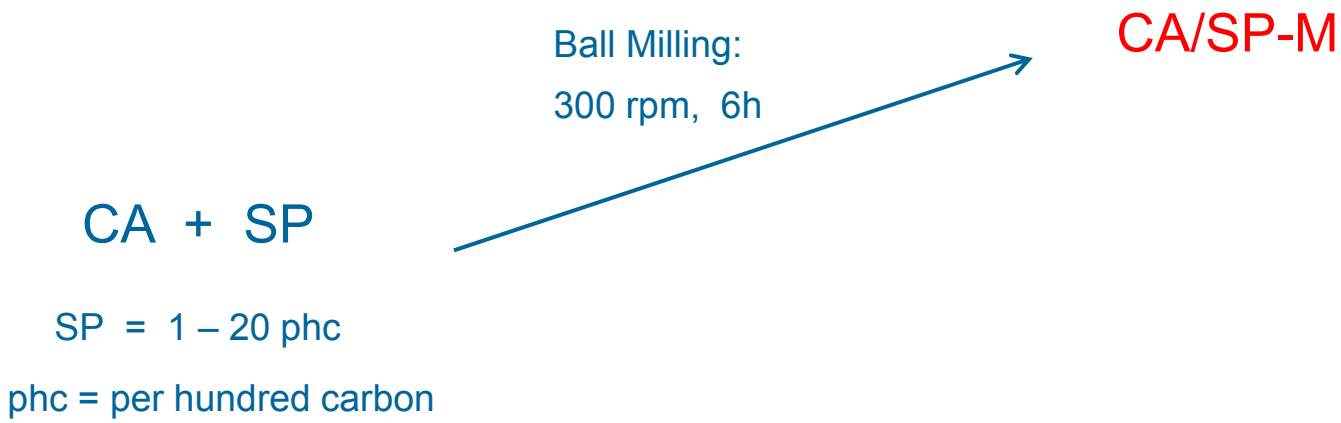
SP = 1 – 20 phc

phc = per hundred carbon

Galimberti, M., Barbera, V., Guerra, S., Conzatti, L., Castiglioni, C., Brambilla, L., A. Serafini, RSC Advances, 5(99), (2015) 81142-81152
Galimberti, M., Barbera, V., Sebastiano, R., Valerio A.M. Leonardi, G.,Citterio, US 2017 0275169 A1
Galimberti M., Barbera V., Guerra S., Bernardi A., Rubber Chemistry and Technology, 2017, 90(2), 285-307.

CA-SP Adducts - Preparation

Mechanical treatment

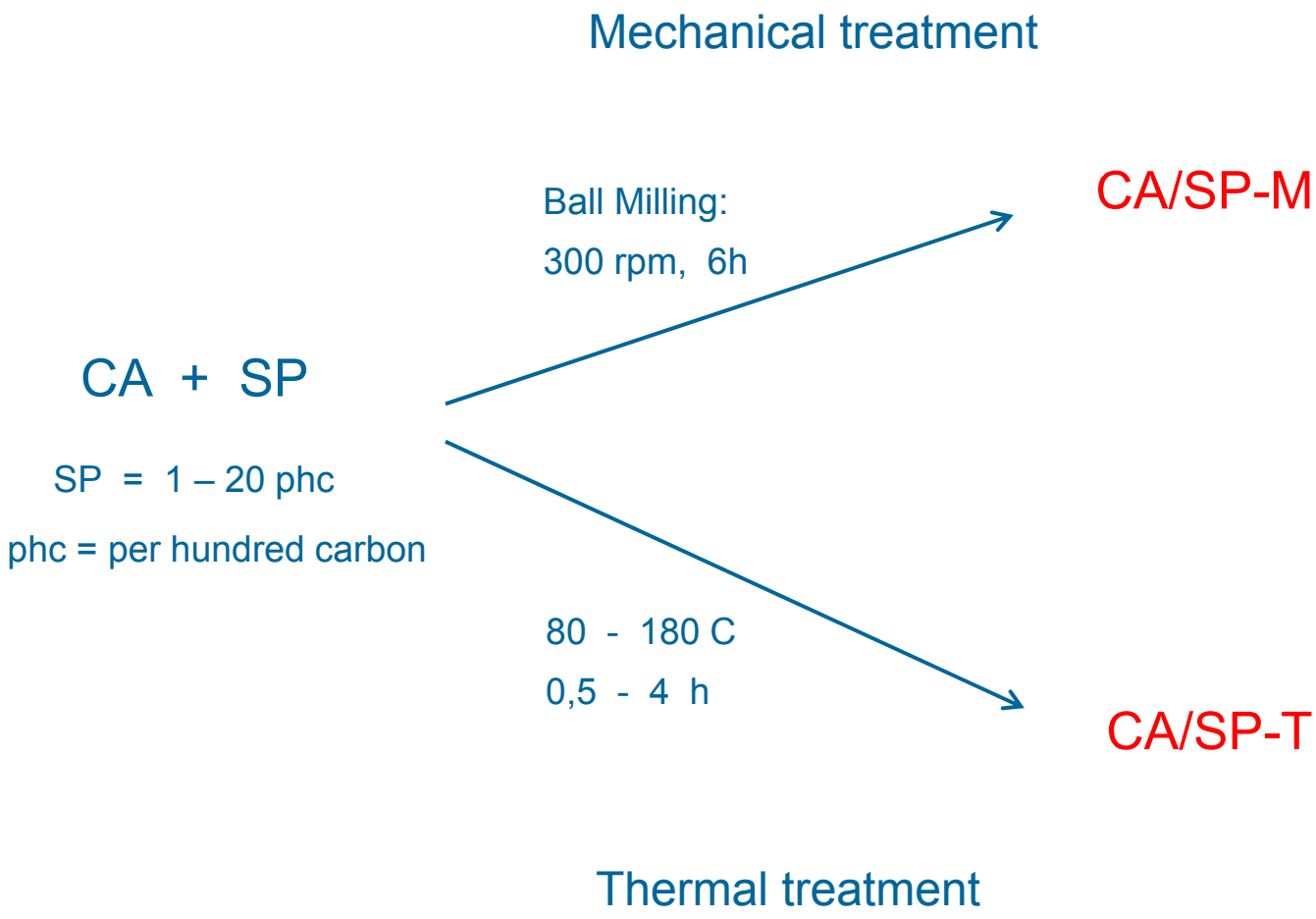


SP = 1 – 20 phc

phc = per hundred carbon

Galimberti, M., Barbera, V., Guerra, S., Conzatti, L., Castiglioni, C., Brambilla, L., A. Serafini, RSC Advances, 5(99), (2015) 81142-81152
Galimberti, M., Barbera, V., Sebastiano, R., Valerio A.M. Leonardi, G.,Citterio, US 2017 0275169 A1
Galimberti M., Barbera V., Guerra S., Bernardi A., Rubber Chemistry and Technology, 2017, 90(2), 285-307.

CA-SP Adducts - Preparation



Galimberti, M., Barbera, V., Guerra, S., Conzatti, L., Castiglioni, C., Brambilla, L., A. Serafini, RSC Advances, 5(99), (2015) 81142-81152
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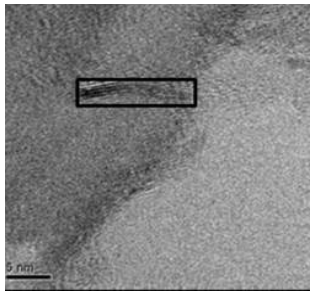
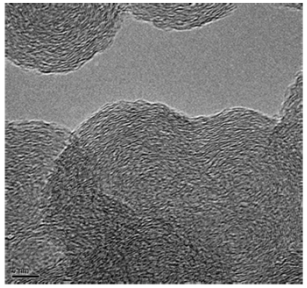
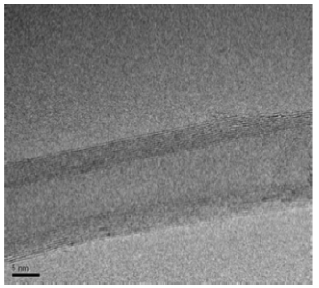
Galimberti M., Barbera V., Guerra S., Bernardi A., Rubber Chemistry and Technology, 2017, 90(2), 285-307.

CA-SP Adducts - Yield of functionalization*

Thermal treatment

SP = 5 phc; 150°C, 2 h

	HSAG	CB	MWCNT
			
BET Surface area: [m^2/g]	300	77	275
Functionalization Yield(%)*:	96	82	92

$$* \text{ Functionalization Yield } (\%) = 100 * \frac{\text{SP mass \% in (CA–SP adduct) after acetone washing}}{\text{SP mass \% in (CA–SP adduct) before acetone washing}}$$

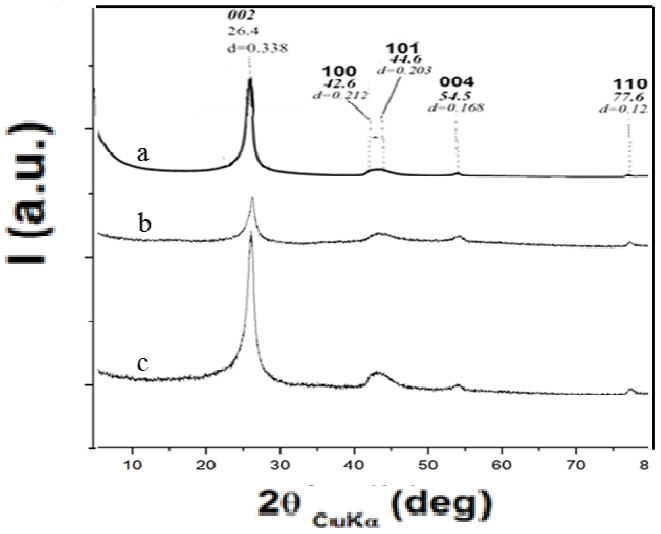
from TGA

HSAG from Asbury, CB from Cabot, CNT from Nanocyl

Adducts of SP with high surface area graphite (HSAG)

CA/SP-T → Soxhlet extraction in acetone

WAXD

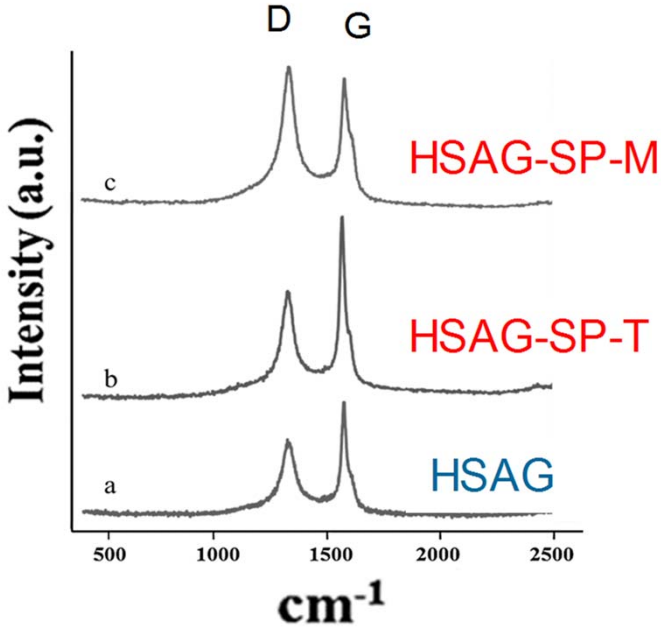


HSAG

HSAG-SP-M

HSAG-SP-T

Raman



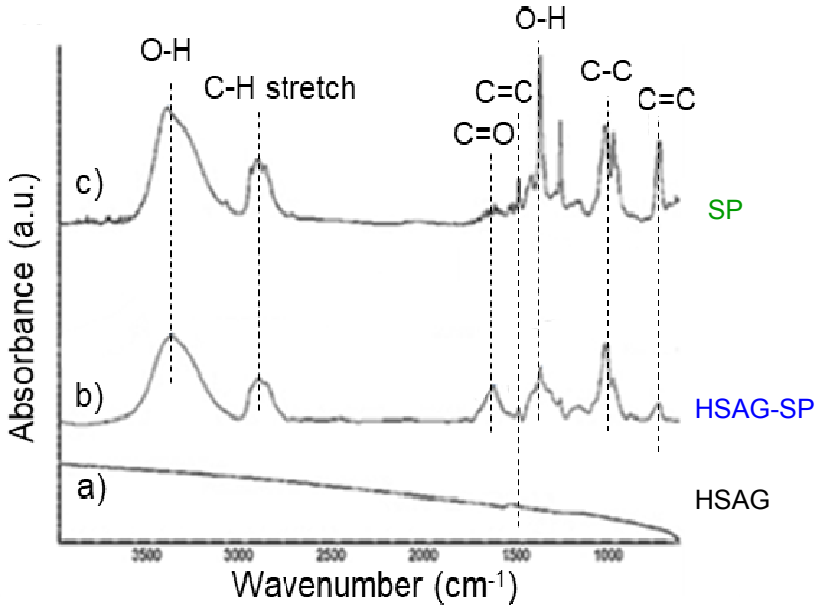
Galimberti, M., Barbera, V., Guerra, S., Conzatti, L., Castiglioni, C., Brambilla, L., A. Serafini, RSC Advances, 5(99), (2015) 81142-81152

Galimberti M., Barbera V., Guerra S., Bernardi A., Rubber Chemistry and Technology, 2017, 90(2), 285-307.

Adducts of SP with high surface area graphite (HSAG)

CA/SP-T → Soxhlet extraction in acetone

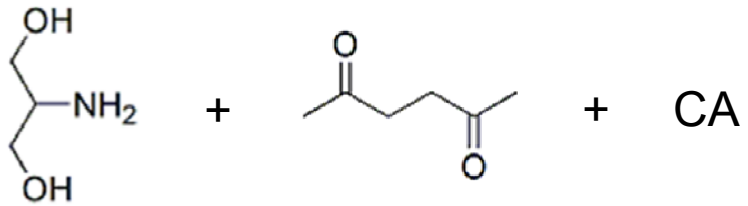
FT-IR



Galimberti, M., Barbera, V., Guerra, S., Conzatti, L., Castiglioni, C., Brambilla, L., A. Serafini, RSC Advances, 5(99), (2015) 81142-81152

Galimberti M., Barbera V., Guerra S., Bernardi A., Rubber Chemistry and Technology, 2017, 90(2), 285-307.

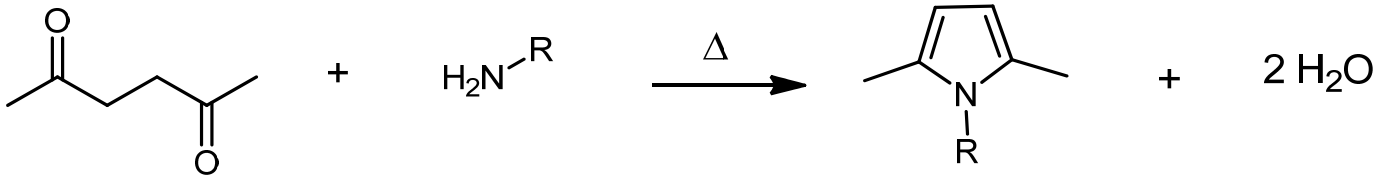
CA-SP Adducts - SP formed *in situ*



CA + SP

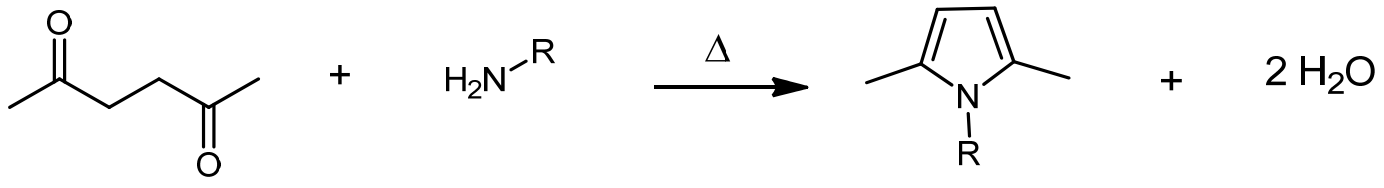
CA-SP adduct

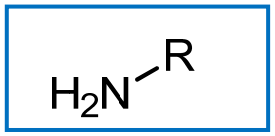
Pyrrole compounds (PyC) from neat Paal Knorr reaction

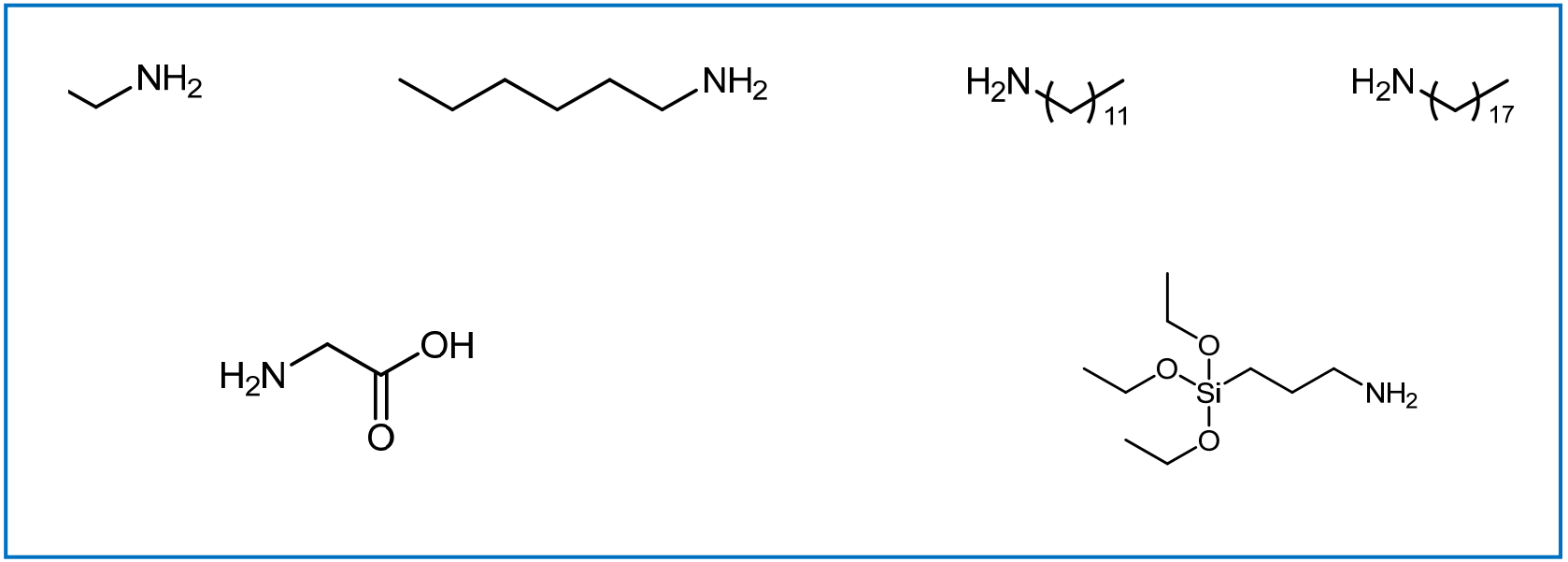


V. Barbera, A. Bernardi, A.Palazzolo, A. Rosengart, L. Brambilla, M. Galimberti Pure and Applied Chemistry 2018, 90(2), 253–270

Pyrrole compounds (PyC) from neat Paal Knorr reaction







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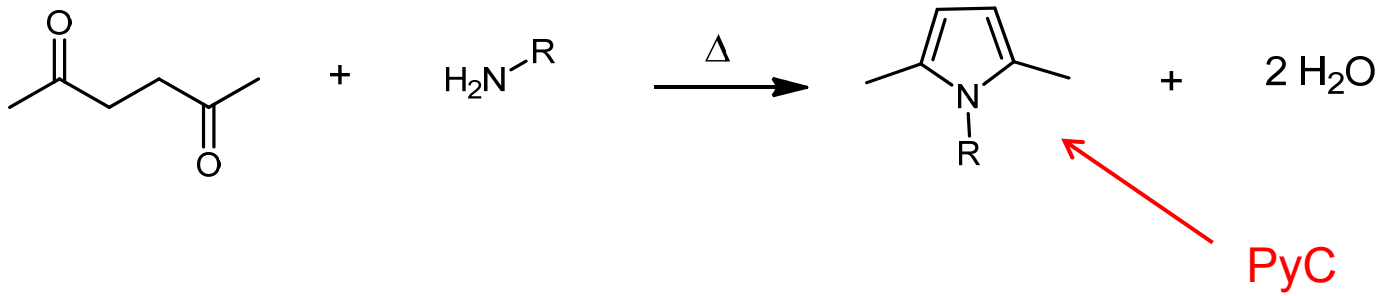
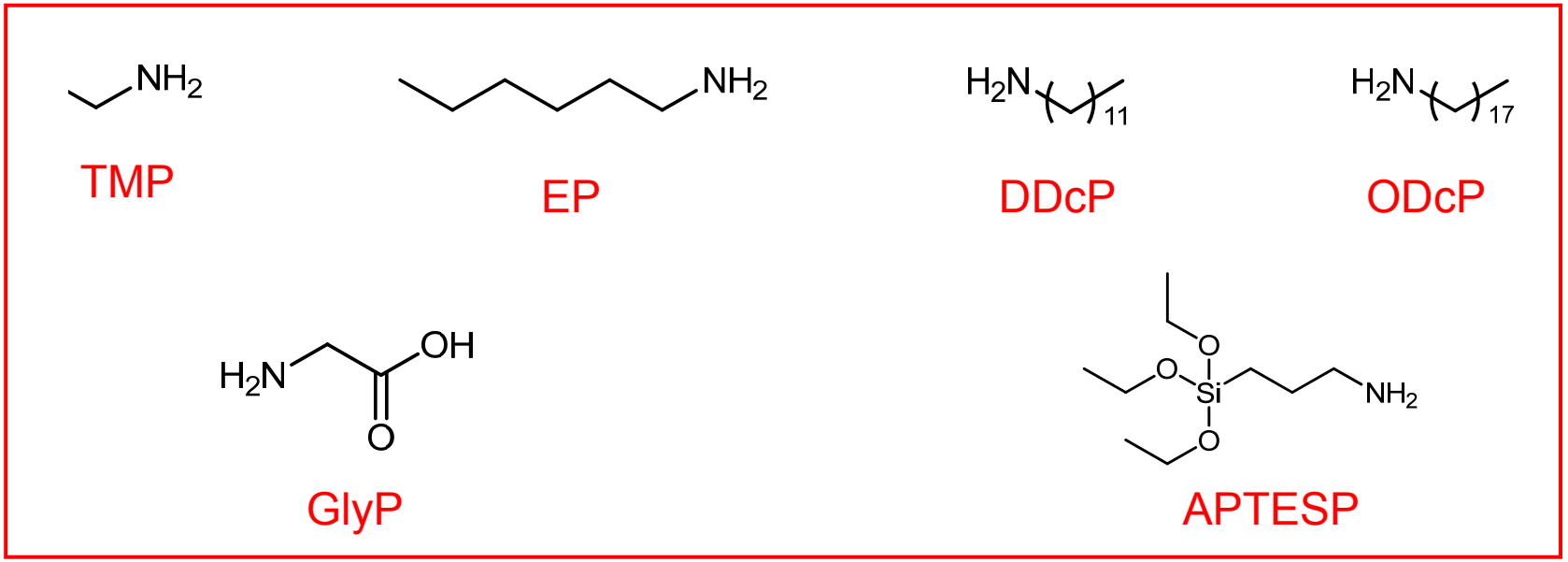
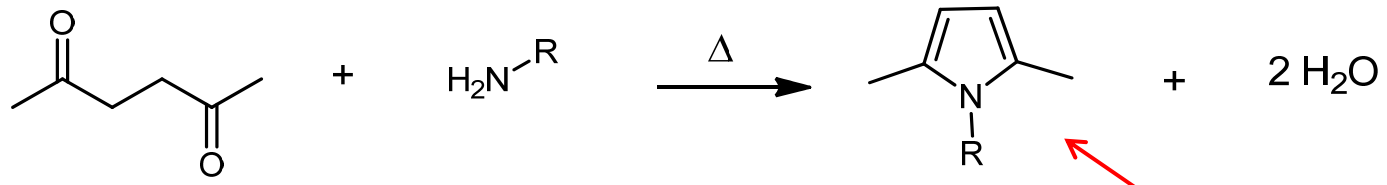




V. Barbera, A. Bernardi, A.Palazzolo, A. Rosengart, L. Brambilla, M. Galimberti Pure and Applied Chemistry 2018, 90(2), 253–270

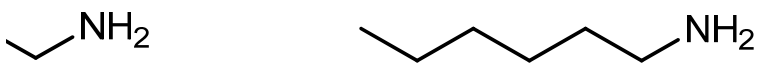
Pyrrole compounds (PyC) from neat Paal Knorr reaction



Same reaction conditions used for SP

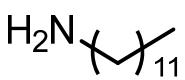
PyC

Yield %

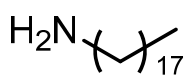


80

75



62



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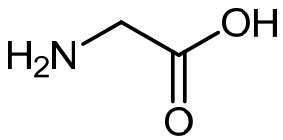

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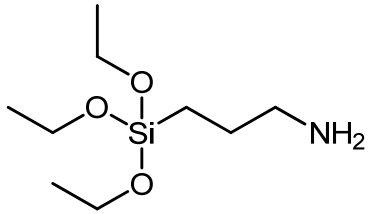
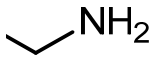


70

V. Barbera, A. Bernardi, A.Palazzolo, A. Rosengart, L. Brambilla, M. Galimberti Pure and Applied Chemistry 2018, 90(2), 253–270

HSAG / PyC adducts

Functionalization Yield %

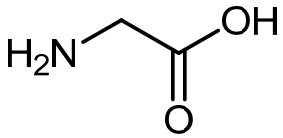


57

53

73

55



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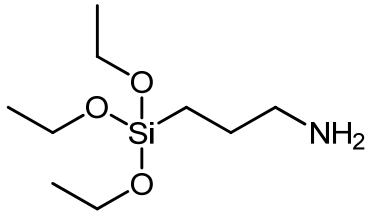
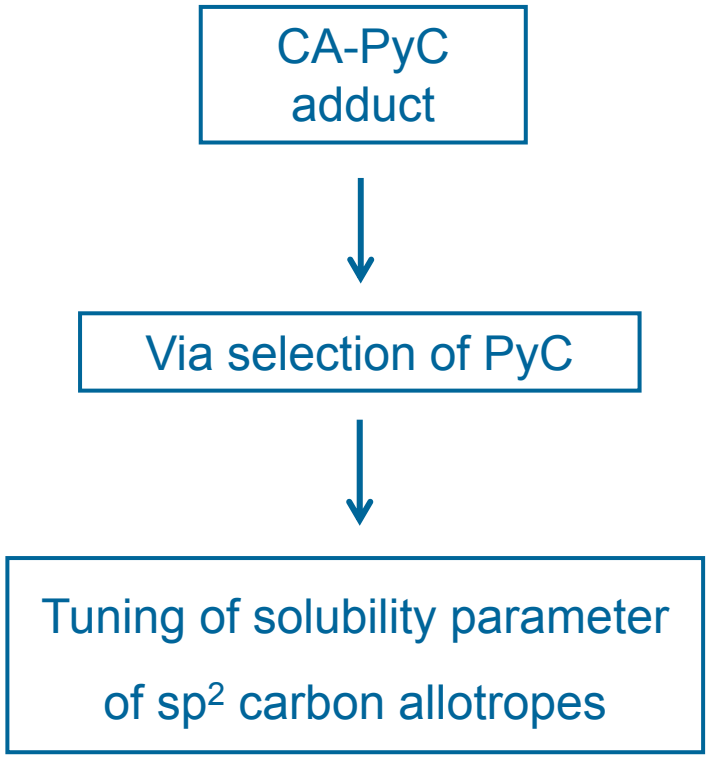


70

V. Barbera, A. Bernardi, A.Palazzolo, A. Rosengart, L. Brambilla, M. Galimberti Pure and Applied Chemistry 2018, 90(2), 253–270

Tuning of solubility parameter of sp^2 carbon allotropes



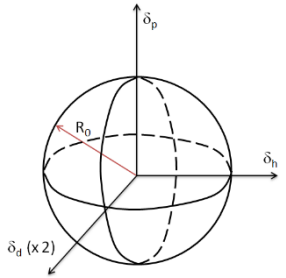
CA / PyC adducts - Tuning of solubility parameters

Experimental determination

Stable suspensions
in solvents
with different δ

Theoretical predictions

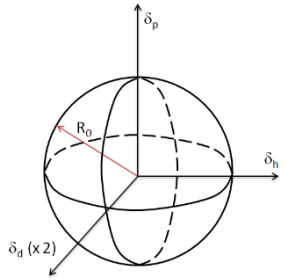
Computational model:
Hansen solubility parameters



Evaluation of solubility parameters of HSAG / PyC adducts

By applying the Hansen Solubility Sphere representation of miscibility

Cohesive energy (Hildebrand model) of a substance:
sum of three contributions:
dispersion, polar, hydrogen bonding:
U_D, U_P, U_H



↓

The substance is identified by three coordinates (δ_D, δ_P and δ_H)
in the Hansen Parameters space

↓

The distance between two points (e.g. of a solute and a solvent)
is related to the cohesive energy difference

↓

Two points close to each other in the Hansen space
indicate miscible substances

Evaluation of HSP of a solute *i*

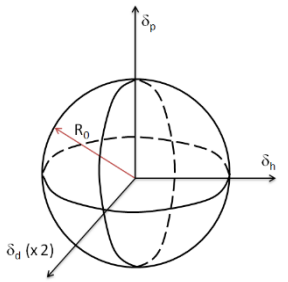
Dispersion tests are performed with different solvents *j*, distinguishing:
- good solvents, which provide stable solutions/dispersions
- bad solvents, which do not give stable dispersions.

↓

Minimization of the ratio * $\dfrac{\text{Distance between the solute and the solvent}}{R_o \text{ radius of interaction}}$

↓

Calculation of the center coordinates of the Hansen solubility sphere



↓

The sphere center coordinates correspond to the three unknown HSP of the solute

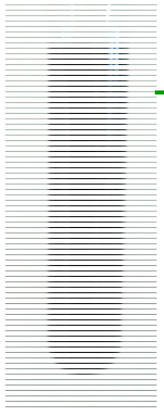
* Fitting sphere program adapted from *J. Polym. Sci. Part B Polym. Phys* **47**(21), 2091 (2009) and solved in Matlab environment using the Nelder-Mead simplex algorithm.

Evaluation of solubility parameters of HSAG-PyC - Experiments

Adduct	solvents				
HSAG-	water	isopropanol	ethyl acetate	toluene	heptane
TMP	bad (↓)	good	good	good	good
EP	bad (↑)	bad (↓)	good	bad (↓)	good
DDcP	bad (↑)	good	good	bad (↓)	bad (↓)
APTESP	bad (↑)	bad (↓)	bad (↓)	good	good
Gly	bad (↓)	good	good	good	bad (↓)
SP	good	good	good	bad (↓)	bad (↓)

No suspension: **bad**

Unstable suspension: **bad**



Stable suspension: **good**

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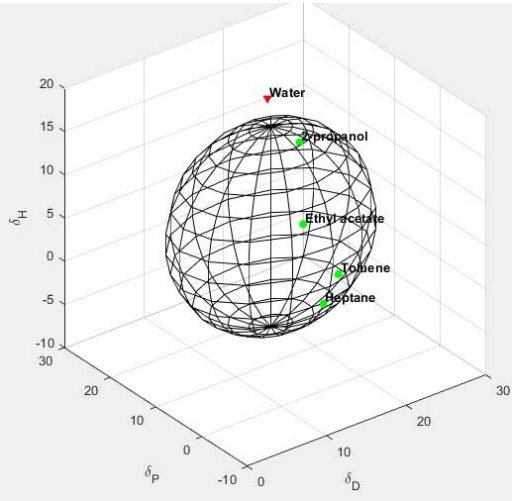
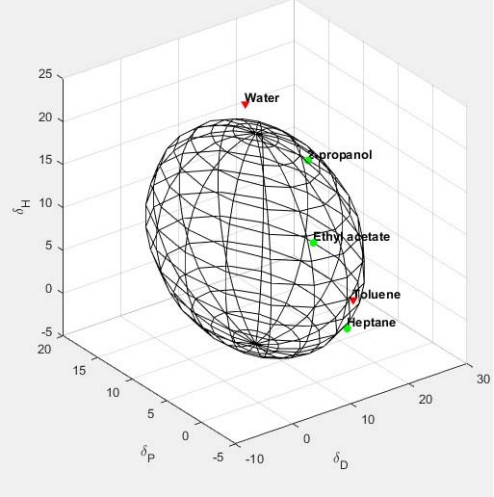
Evaluation of solubility parameters of HSAG-PyC - Hansen sphere

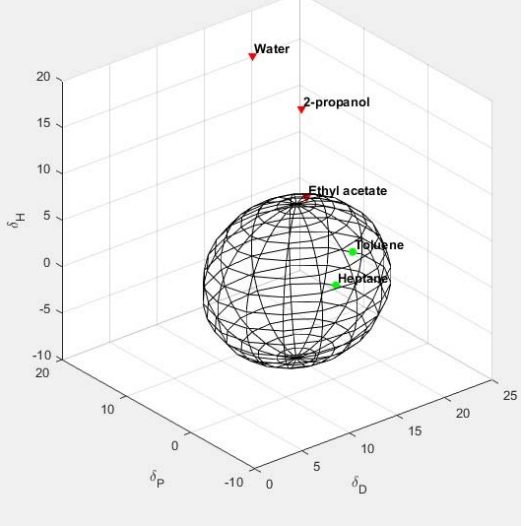
HSAG-TMP



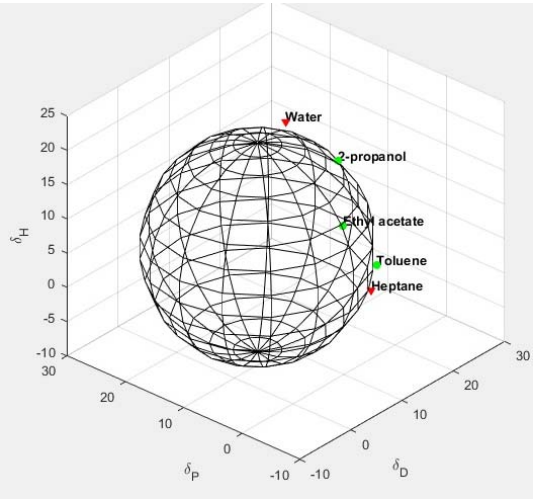
HSAG-DDcP



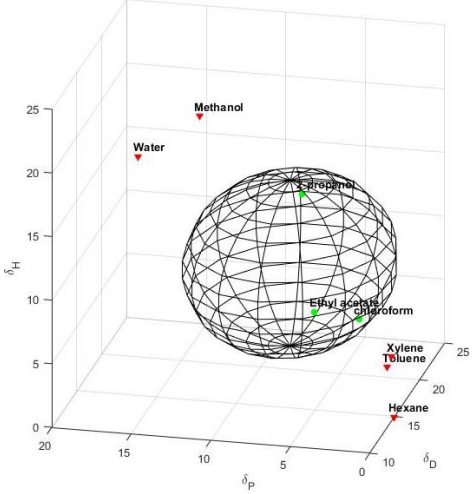
HSAG-APTESP

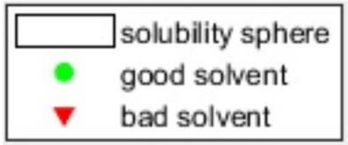


HSAG-GlyP



HSAG-SP



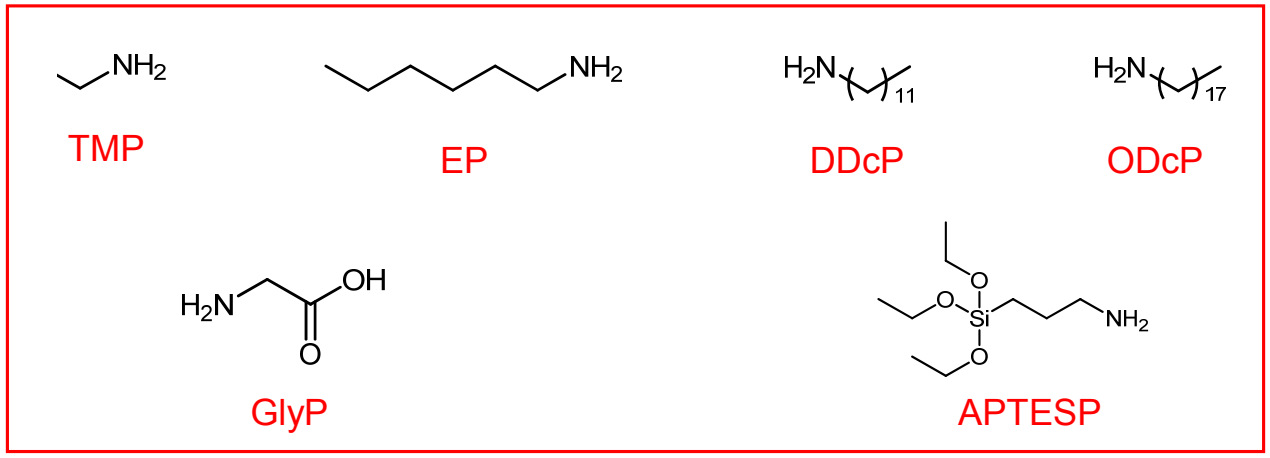


V. Barbera, A. Bernardi, A.Palazzolo, A. Rosengart, L. Brambilla, M. Galimberti Pure and Applied Chemistry 2018, 90(2), 253–270

Evaluation of solubility parameters of HSAG-PyC - δ values

Sample	δ_D	δ_P	δ_H	Radius
HSAG	17.8	3.1	5.7	1.0
HSAG-TMP	14.6	10.3	5.6	11.6
HSAG-DDcP	8.5	7.5	8.3	12.3
HSAG-APTESP	12.7	2.3	0.5	8.3
HSAG-SP	12.8	2.0	8.9	13.8
HSAG-GlyP	6.9	12.1	5.3	15.3

Amount of PyC on HSAG: about 5% mol



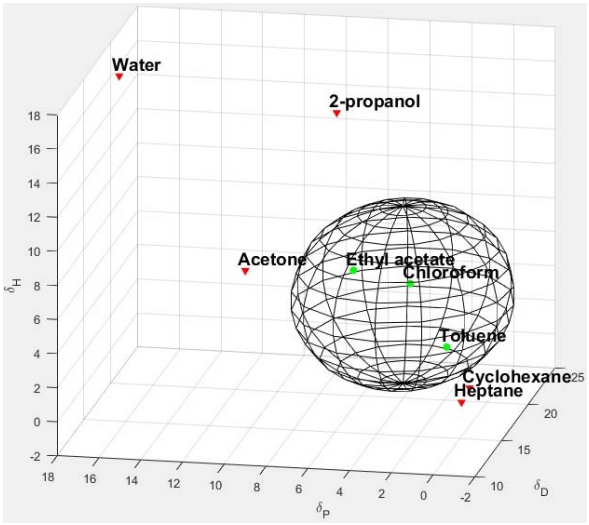
V. Barbera, A. Bernardi, A.Palazzolo, A. Rosengart, L. Brambilla, M. Galimberti Pure and Applied Chemistry 2018, 90(2), 253–270

Evaluation of solubility parameters of CB-PyC - Experiments

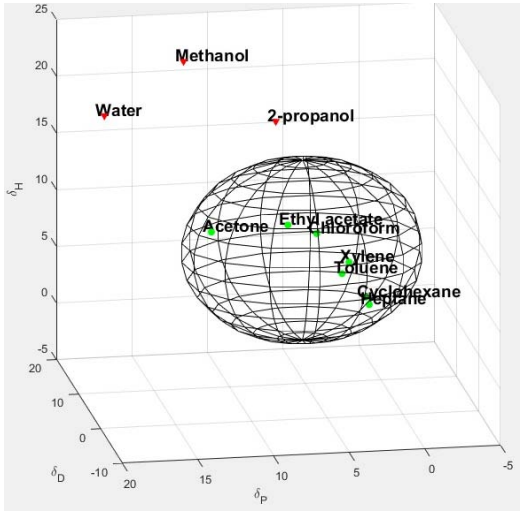
Adduct	Solvents										
CB-	Hexane	Heptane	Cyclohexane	Toluene	Xylene	Chloroform	Ethyl acetate	Acetone	2-propanol	Methanol	H_2O
=	Bad	Bad	Bad	Bad	Bad	Good	Good	Bad	Good	Bad	Bad
TMP	Bad	Bad	Bad	Bad	Bad	Good	Good	Bad	Bad	Bad	Bad
ODcP	Good	Bad	Good	Good	Good	Good	Good	Good	Bad	Bad	Bad
APTESP	Bad	Bad	Bad	Good	Good	Good	Good	Good	Bad	Bad	Bad
SP	Bad	Bad	Bad	Bad	Good	Good	Good	Good	Good	Bad	Good
GlyP	Bad	Bad	Bad	Bad	Bad	Good	Good	Good	Good	Bad	Good

Evaluation of solubility parameters of CB-PyC - Hansen sphere

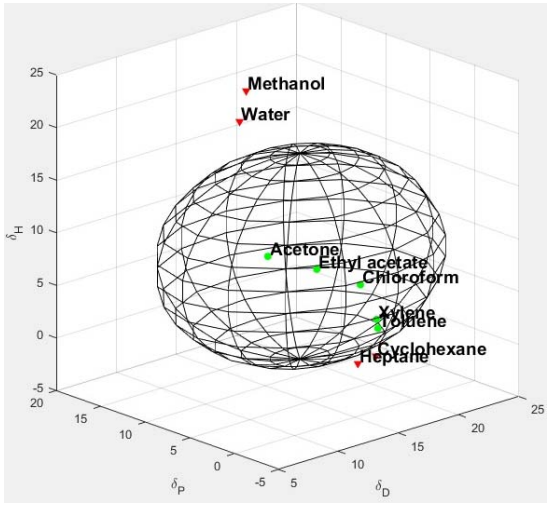
CB-TMP



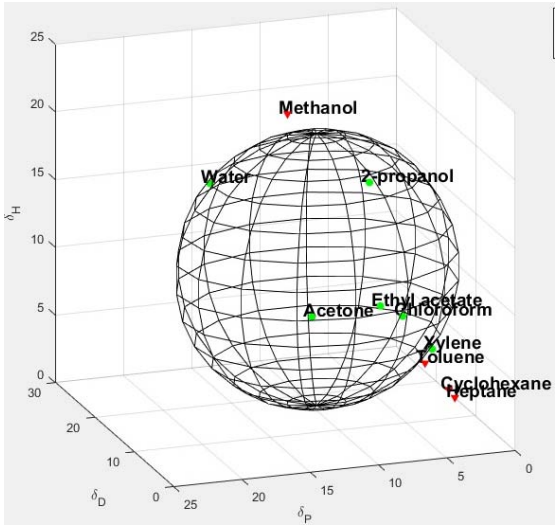
CB-ODcP

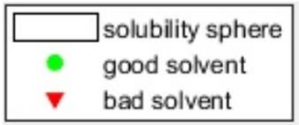


CB-APTESP

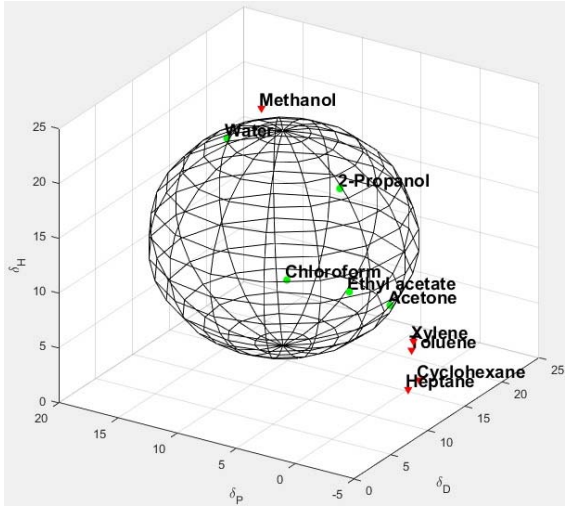


CB-SP





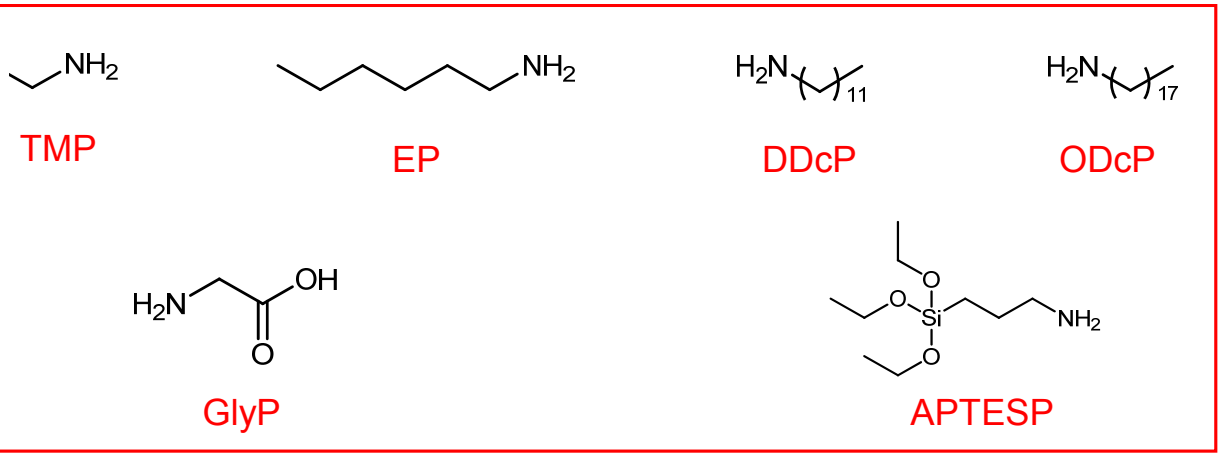
CB-GlyP



Evaluation of solubility parameters of CB-PyC - δ values

Sample	δ_D	δ_P	δ_H	Radius
CB N234	16.8	7.1	10.3	6.5
CB-TMP	18.1	3.5	4.9	5.2
CB-ODcP	6.4	5.7	7.9	7.9
CB-APTESP	14.9	6.0	8.5	9.8
CB-SP	11.8	11.1	11.5	10.1
CB-GlyP	12.1	8.6	12.8	9.8

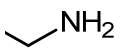
Amount of PyC on CB: about 10% mass



Evaluation of solubility parameters of CNT-PyC - δ values

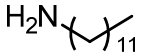
Sample	δ_D	δ_P	δ_H	Radius
CNT-TMP	17.9	5.1	9.3	10.3
CNT-DDcP	6.7	10.6	13.4	10.6
CNT-APTESP	20.9	13.1	5.3	10.9
CNT-SP	20.9	12.1	10.3	13.3
CNT-GlyP	12.0	11.8	15.7	18.7

Amount of PyC on CNT: about 5% mol

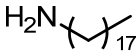


TMP

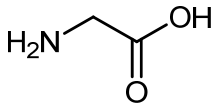
EP



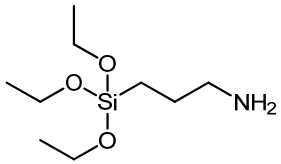
DDcP



ODcP

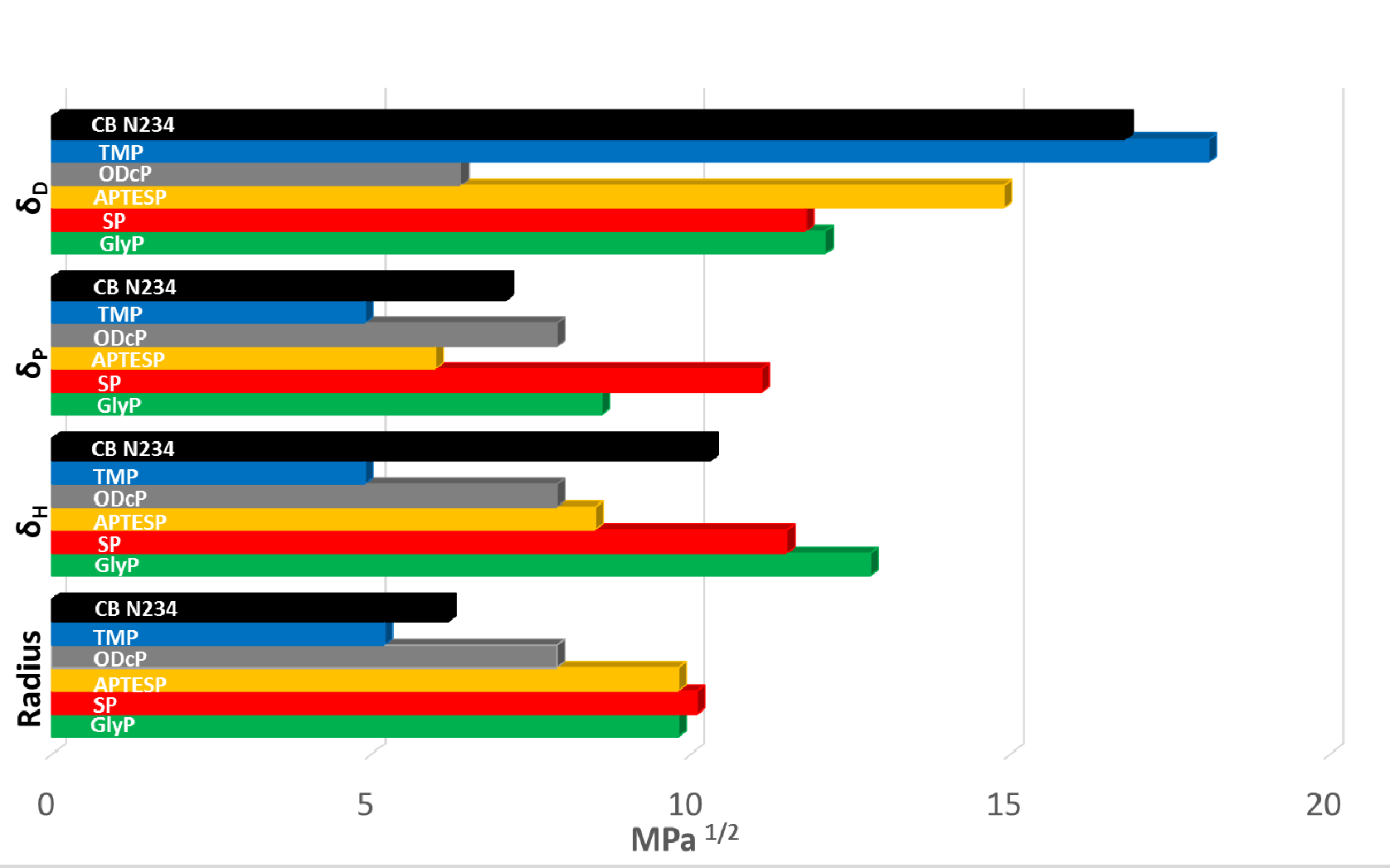


GlyP



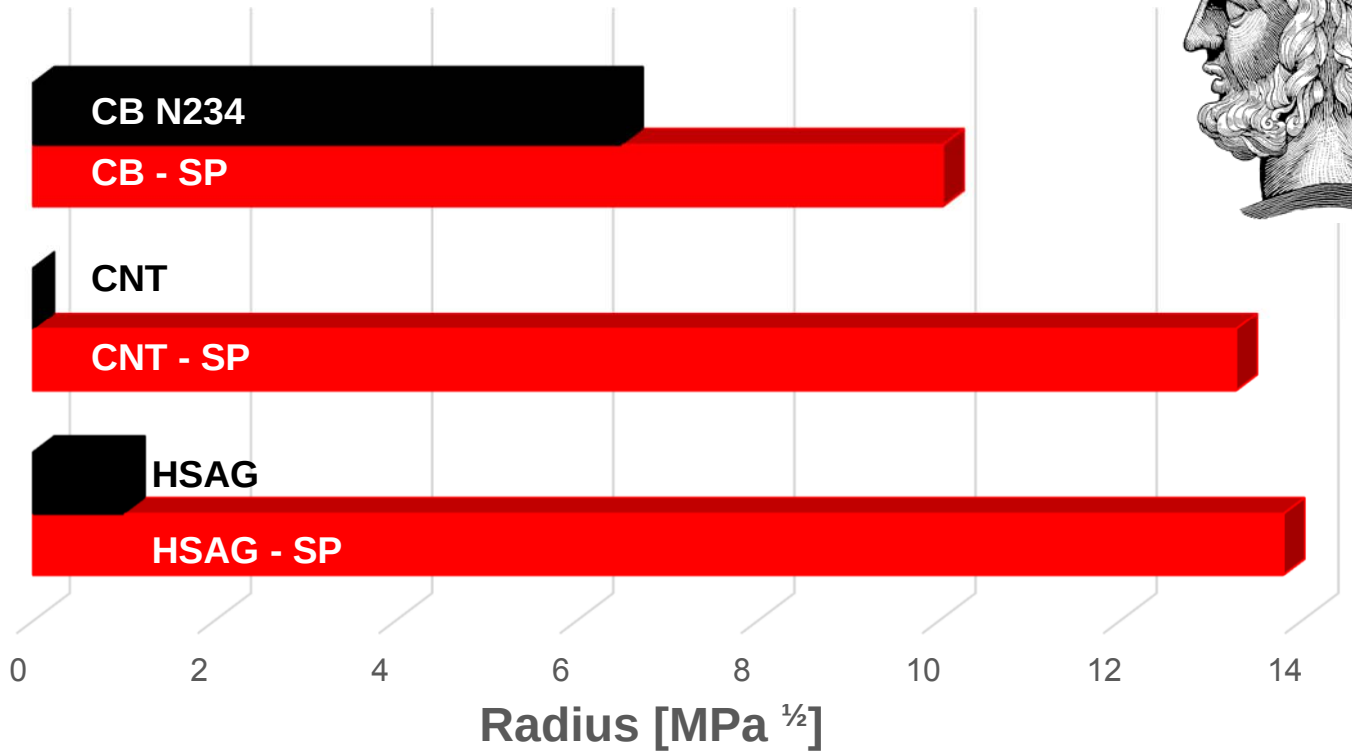
APTESP

Evaluation of solubility parameters of CB-PyC - comparison



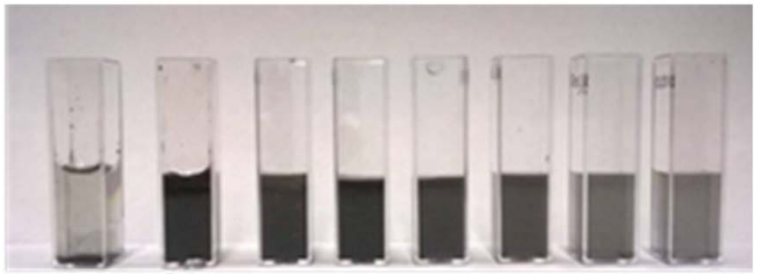
Amount of PyC on CB: 10 mass%

Evaluation of solubility parameters of CA-SP - Radius comparison



(*) Amount of SP on CA: 10 mass%

Water dispersions of HSAG-SP adducts



conc: from 10 to 0.1 mg/mL

Conductive inks

From 0.1 to 200 g/L

NR/HSAG composites - Electrical conductivity

NR latex dispersion of HSAG

↓

Addition of vulcanizers via melt blending

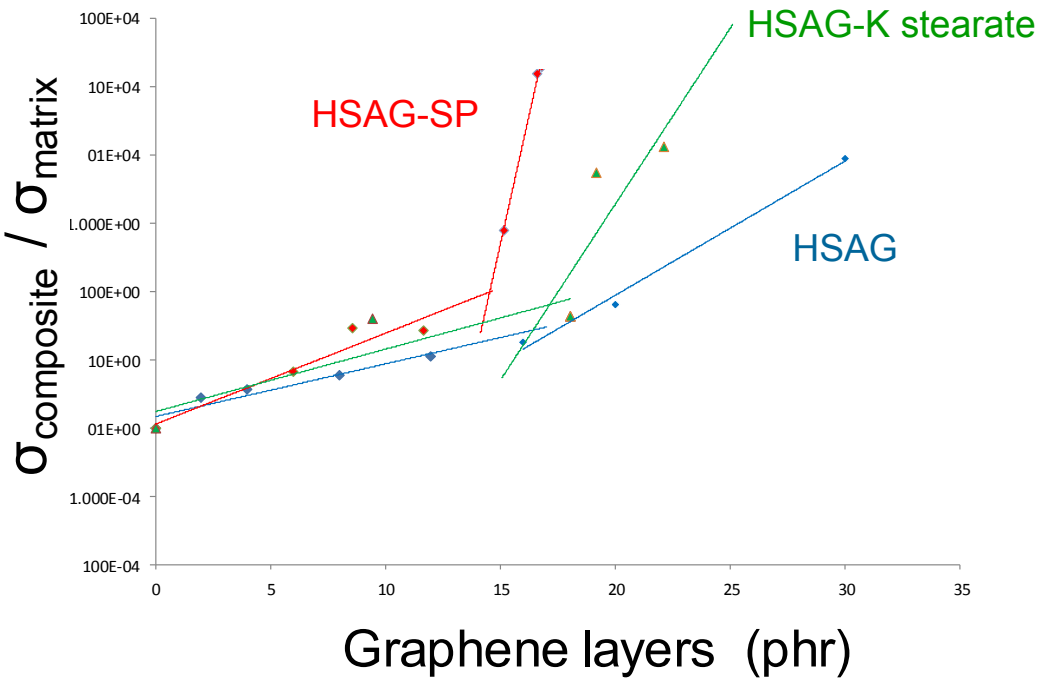
↓

Vulcanization

↓

Electrical conductivity

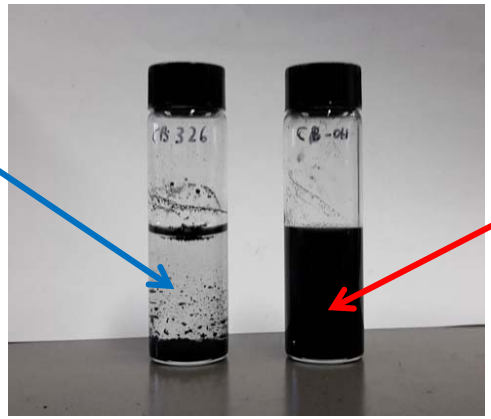
Electrical conductivity



Water dispersions of CB-SP adducts

CB/SP + Water ⟶ Stirring or sonication

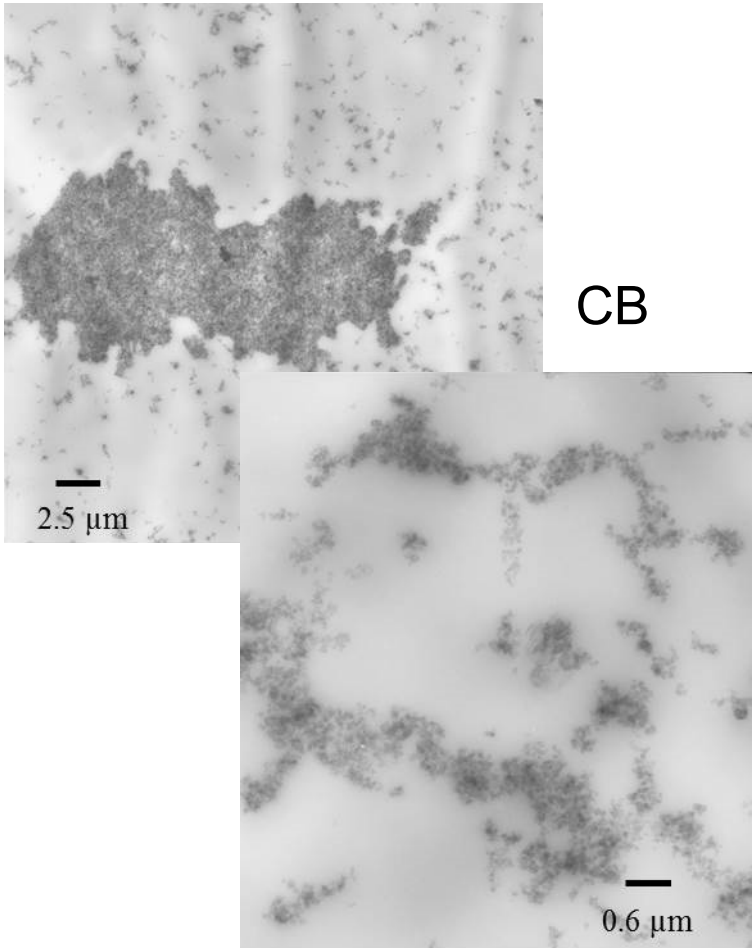
CB in water



CB-OH
in water

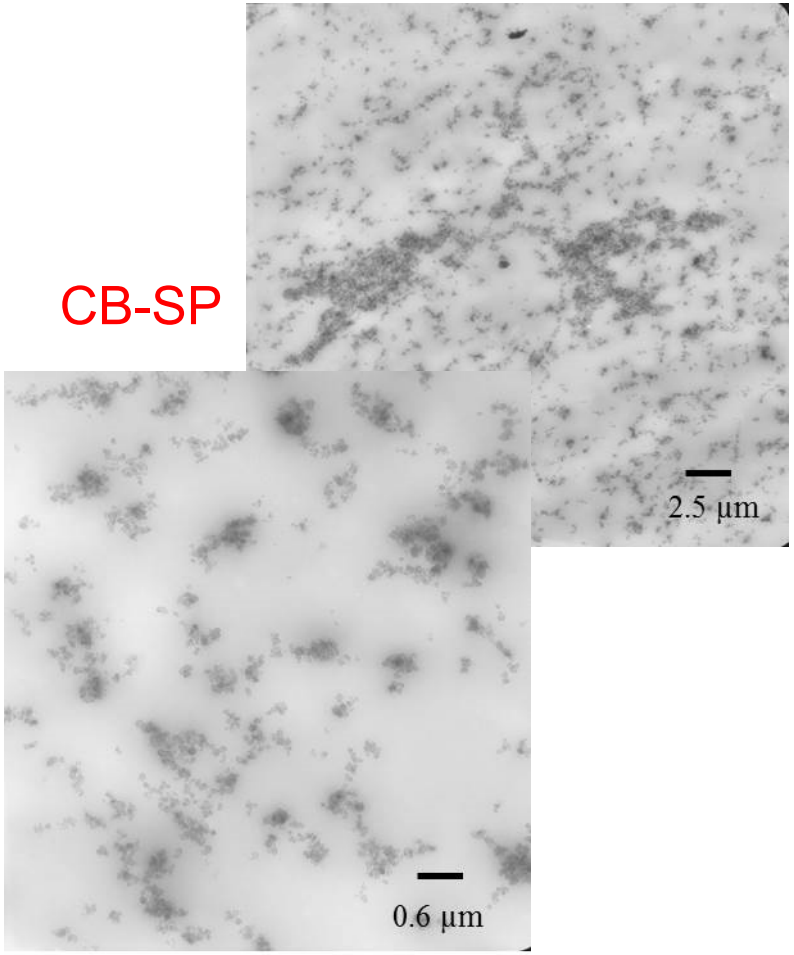
Composites form NR latex dispersions of CB-SP adducts

TEM

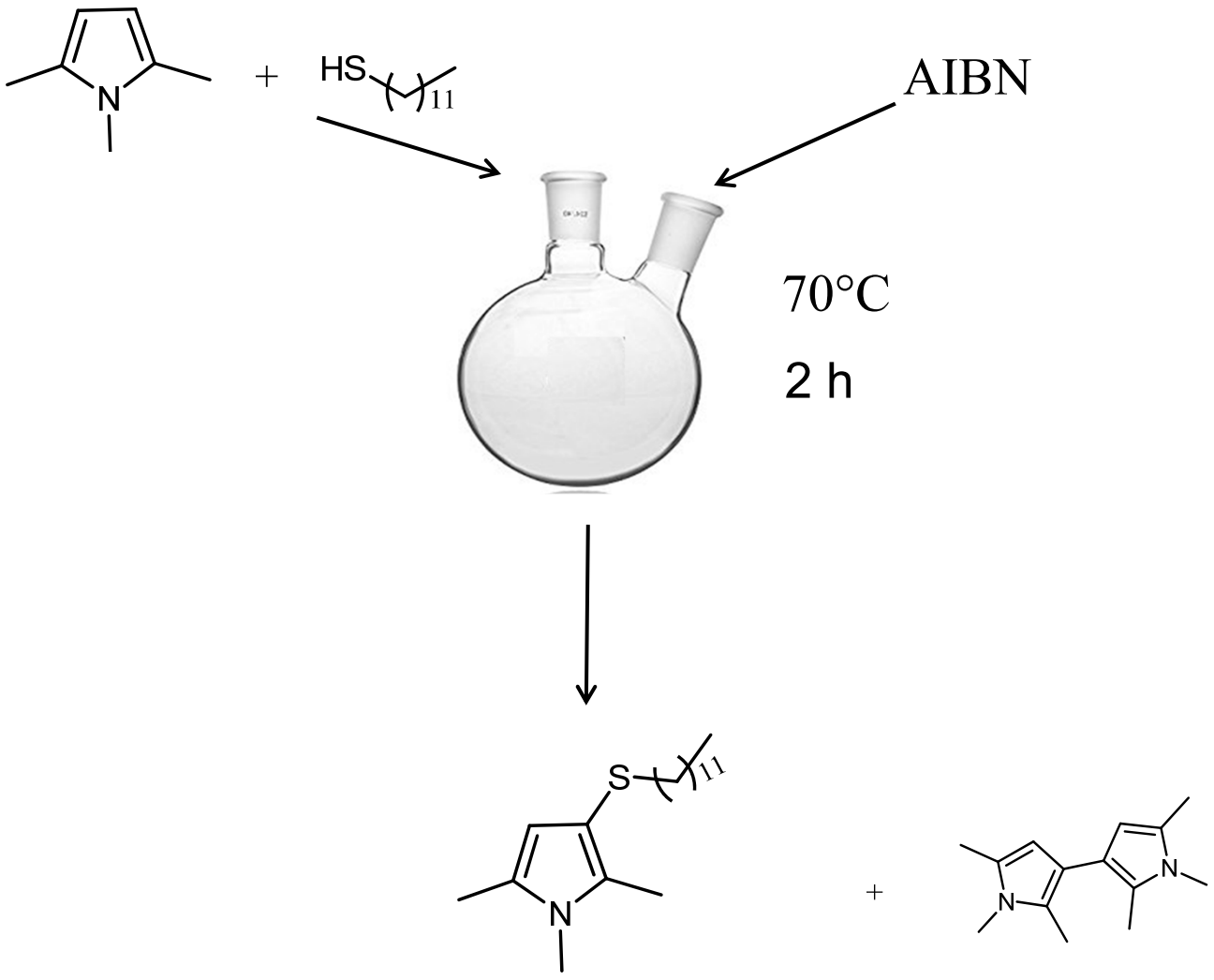


CB

CB-SP



Reactivity with sulphur



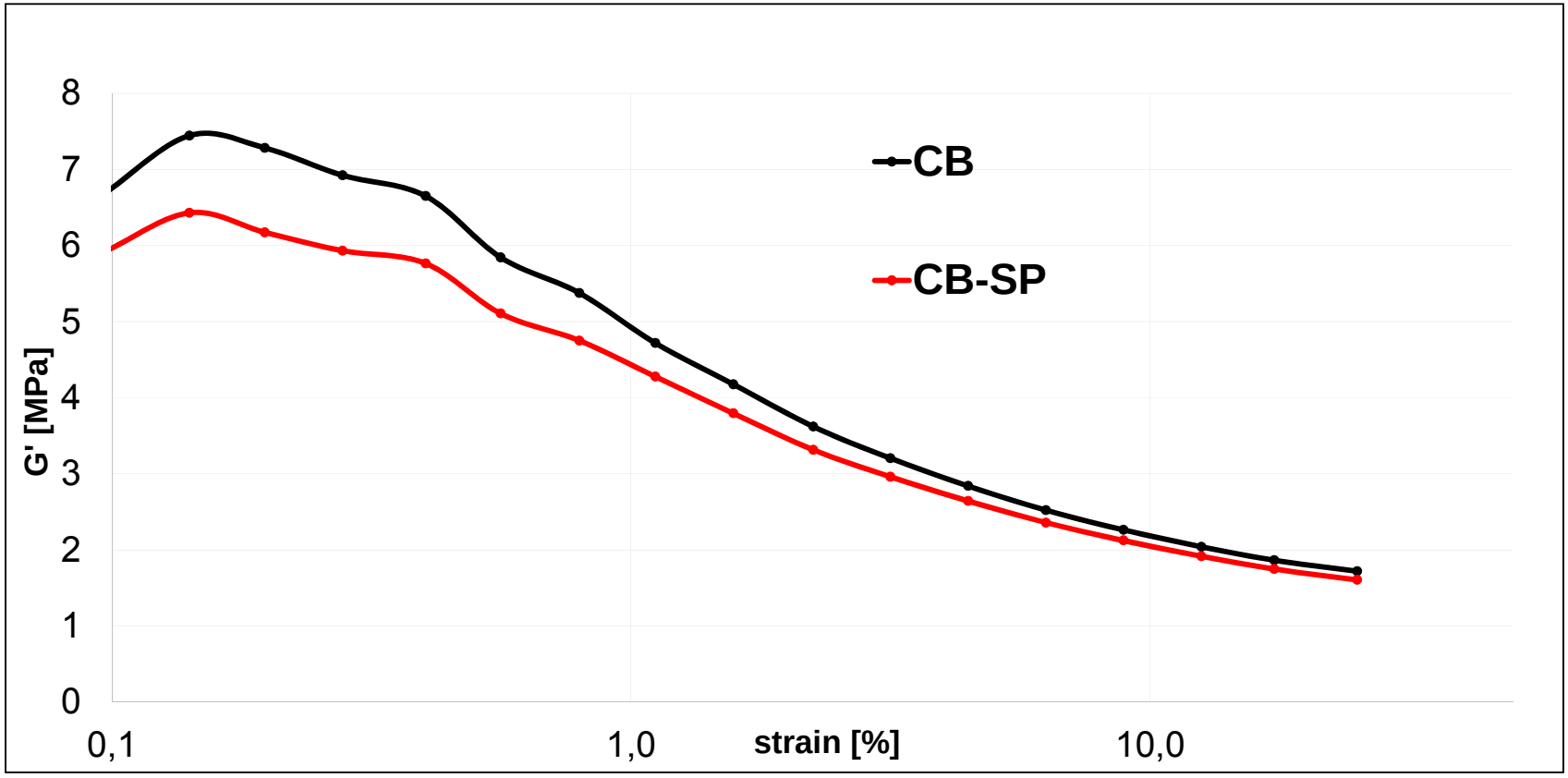
NR based compounds with CB-SP

Compound with:	CB	CB-SP
NR	100,00	100,00
CB N234	60,00	0,00
CB-SP	0,00	62,40
Ac Stearico	2,00	2,00
ZnO	4,00	4,00
6PPD	2,00	2,00
TBBS	1,80	1,80
Sulphur	1,80	1,80

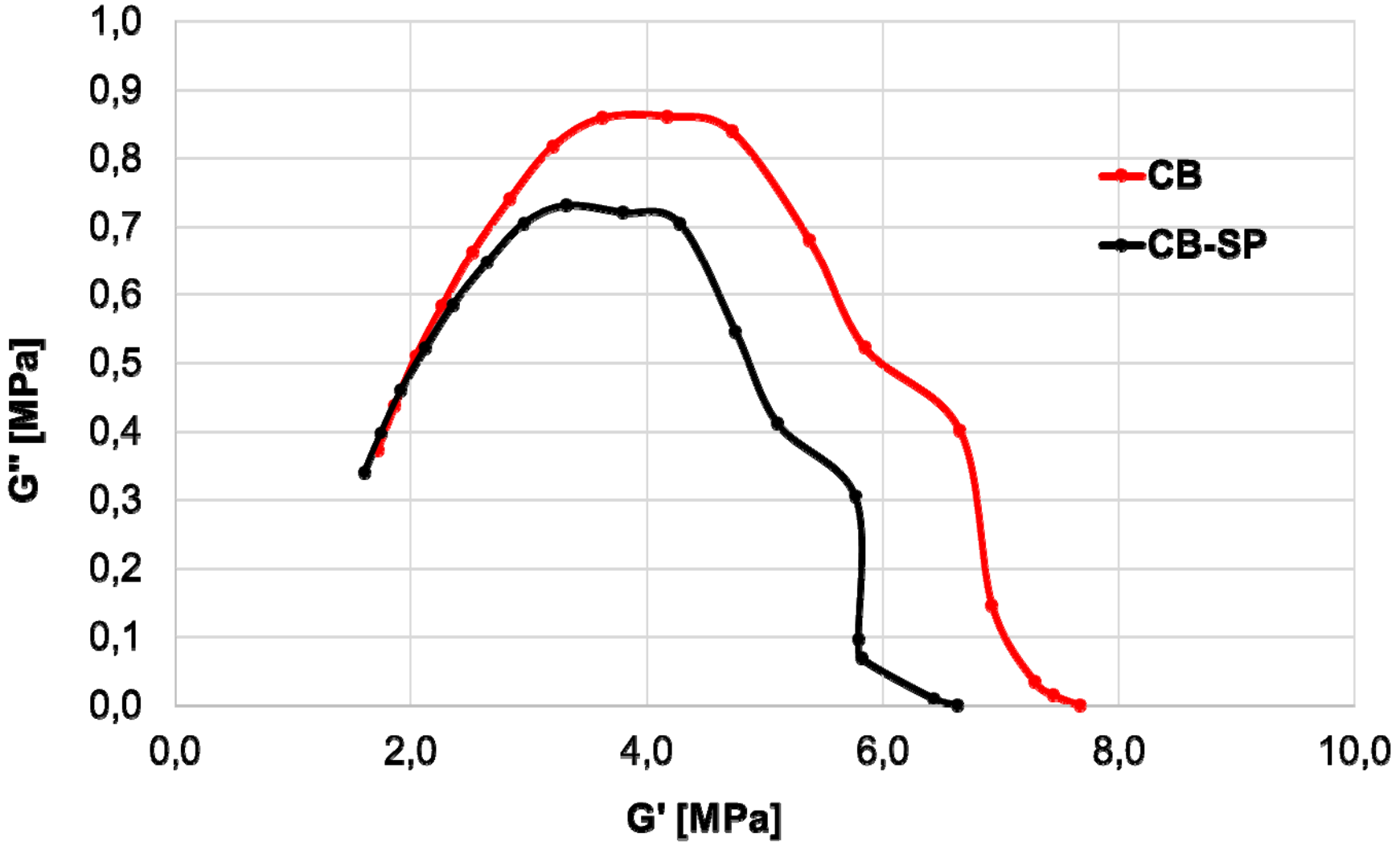
Amounts in phr Melt blending

NR based compounds with CB-SP

G' vs strain



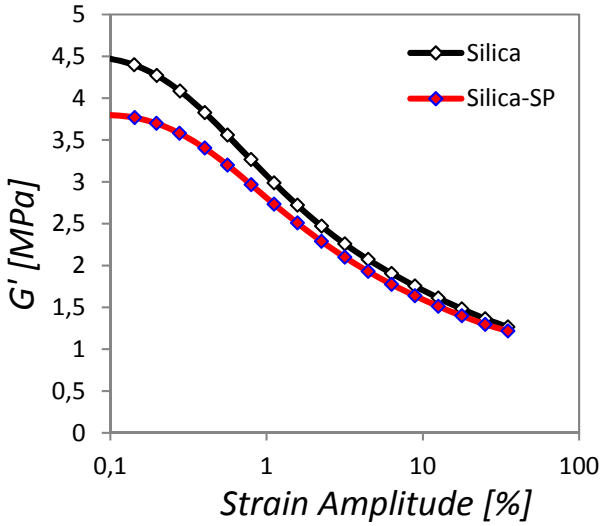
NR based compounds with CB-SP

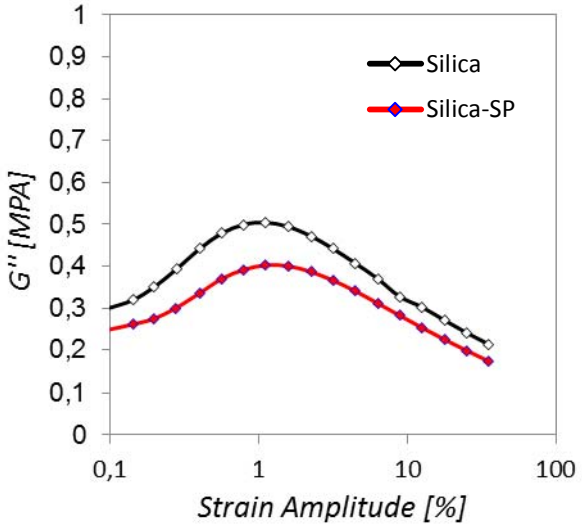


CB/SP adducts in silica based composites for lower dissipation of energy

Ingredients	without SP	with SP
IR	100	100
CB	30	30
Silica	30	30
SP	0	3

ZnO 4.0, Stearic acid 2.0, 6PPD 2.0, Sulphur 3, TBBS 1.8





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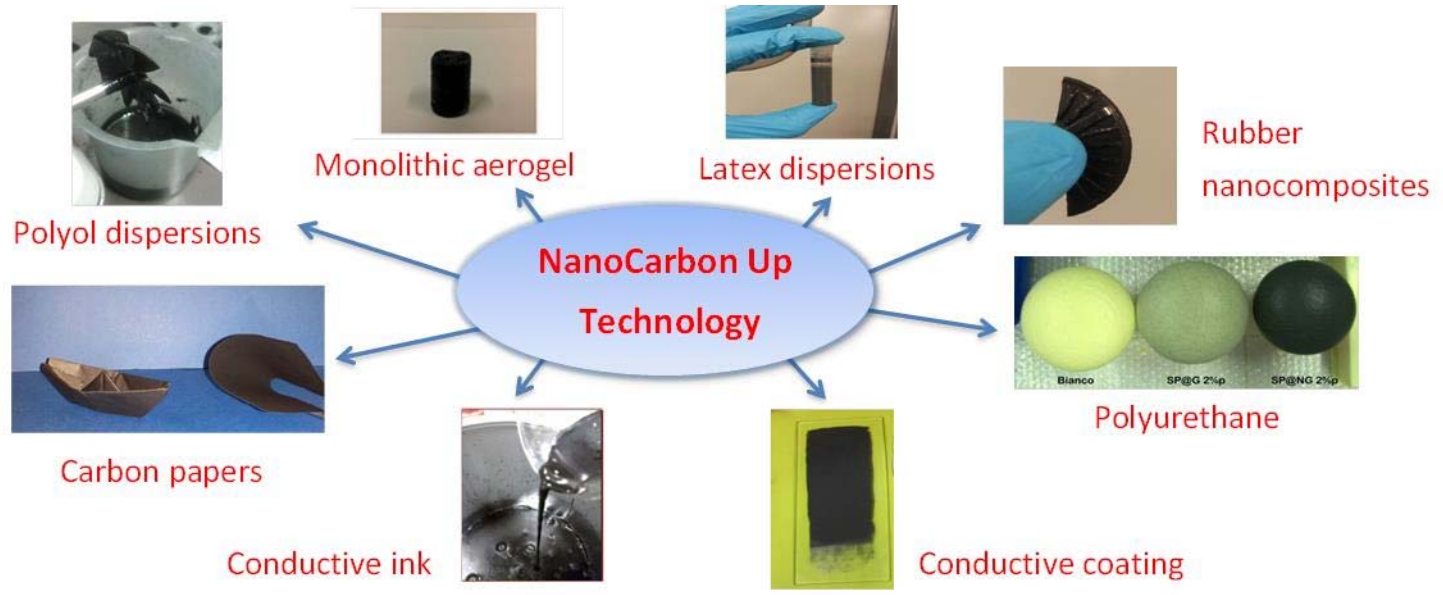
NanoCarbon Up Technology



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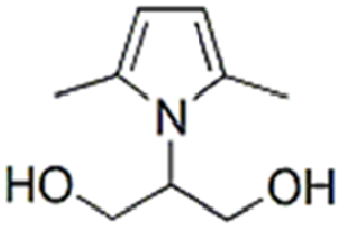
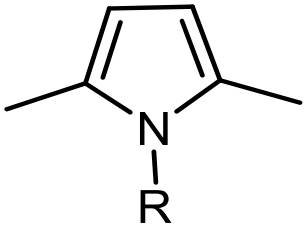
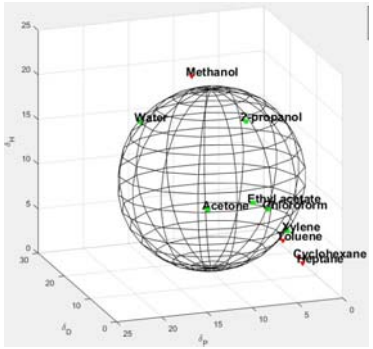
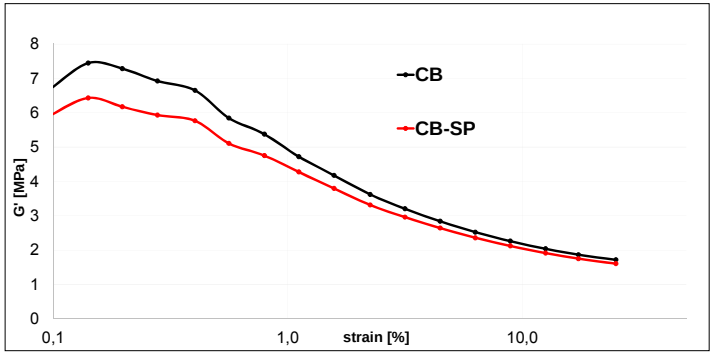
Conclusions









Thanks
for the attention!

*Enhancing science, technology and business across the **evolving elastomeric community**.*