Sustainable and versatile functionalization of graphene layers

Maurizio Galimberti

Vincenzina Barbera, Andrea Bernardi, Daniele Locatelli, Gea Prioglio

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

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Innovative Sustainable Chemistry and Materials and Proteomics Group

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Items of the presentation

- Objective of the research
- Strategy: sustainability for innovation
- Janus molecules for the functionalization of graphene layers
- Properties of functionalized graphene layers
- Applications

Objective of the research

Polymer composites

Lead to the macroscopic scale the exceptional properties of graphene and graphene related materials

Carbocatalysts

Are ideal when are characterized by:

high surface areas and large unperturbed aromatic basal planes

Objective of the research

Sustainable and versatile functionalization

of unperturbed graphene layers

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)

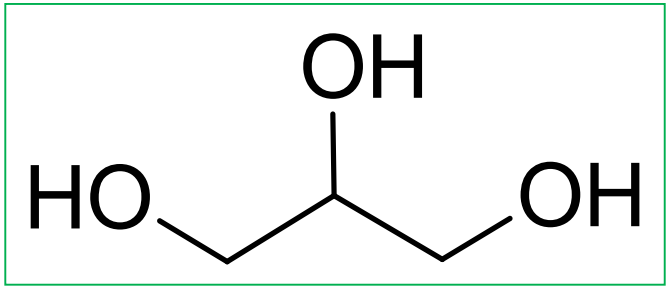
Xylitol/arabinitol (Sugar alcohols from xylose and arabinose)

Glutamic acid

Levulinic acid

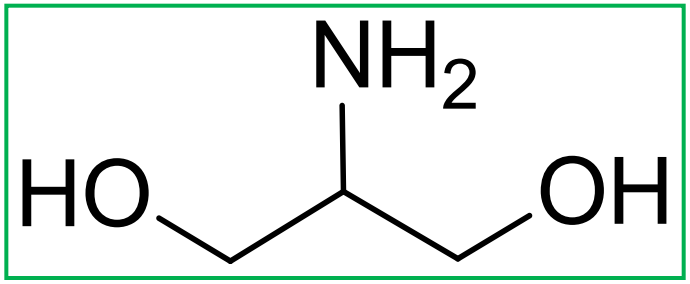
DOE = US Department of Energy

Glycerol



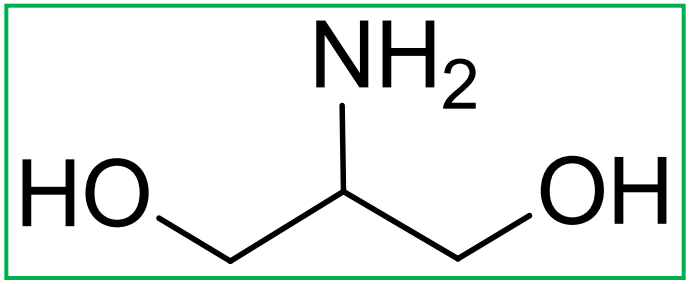
- easily available, cheap raw material
- main by-product of bio-diesel production
- not toxic
- biodegradable

Glycerol derivative: serinol



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

Glycerol derivative: serinol



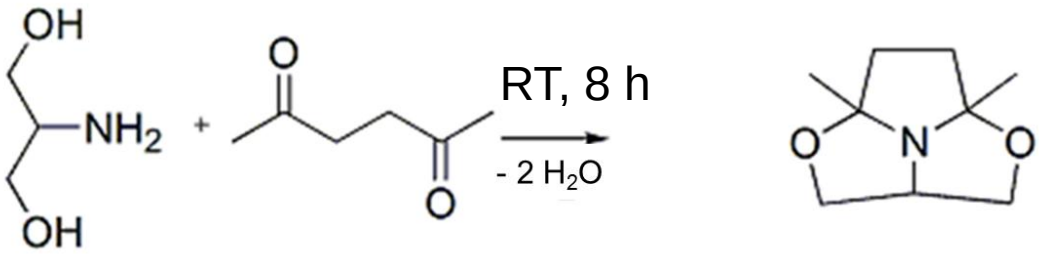
- Starting building block for many reaction pathways: many derivatives

- Chemoselectivity

↓

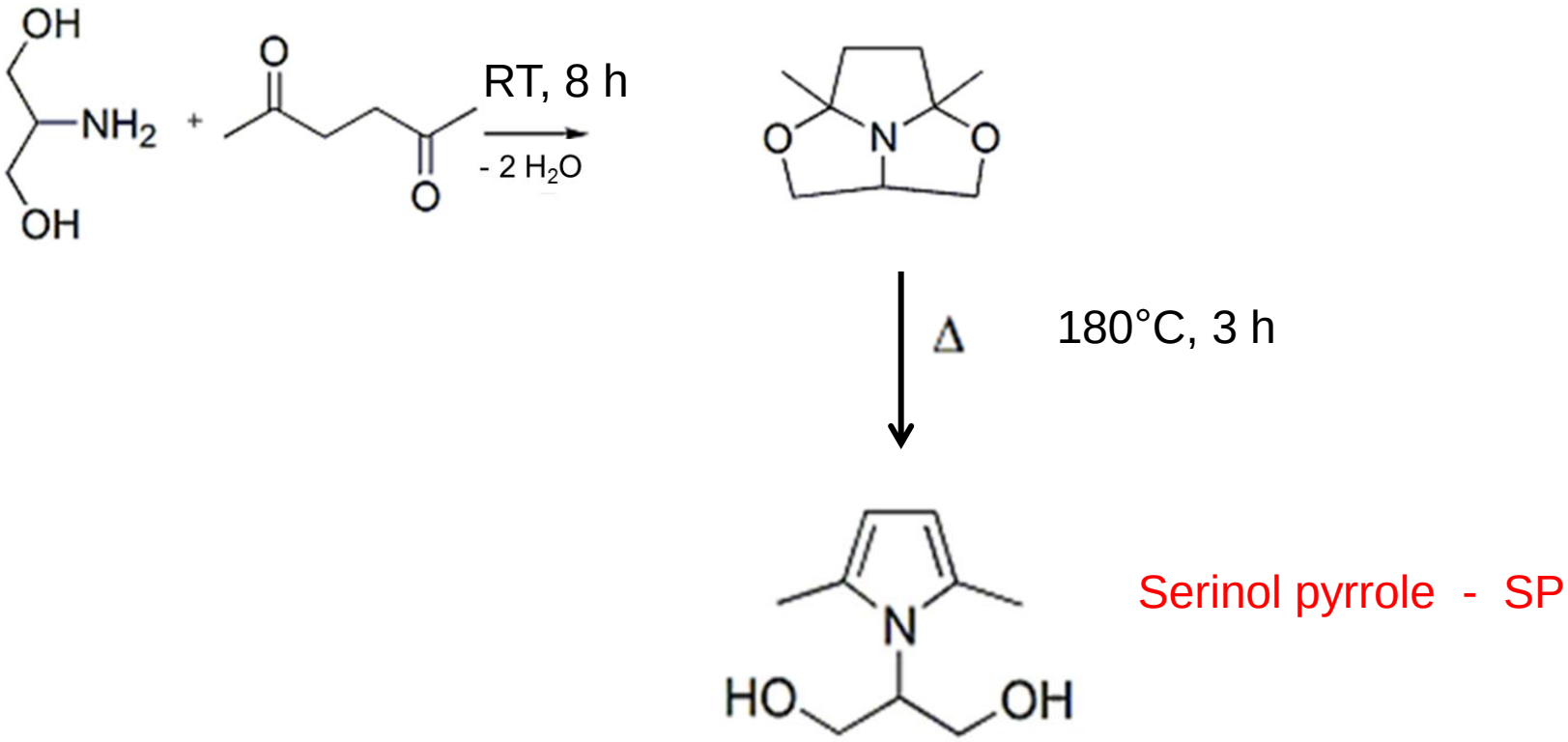
Reactions of the amino group with carbonyl compounds

Specific 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

From serinol to serinol pyrrole



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

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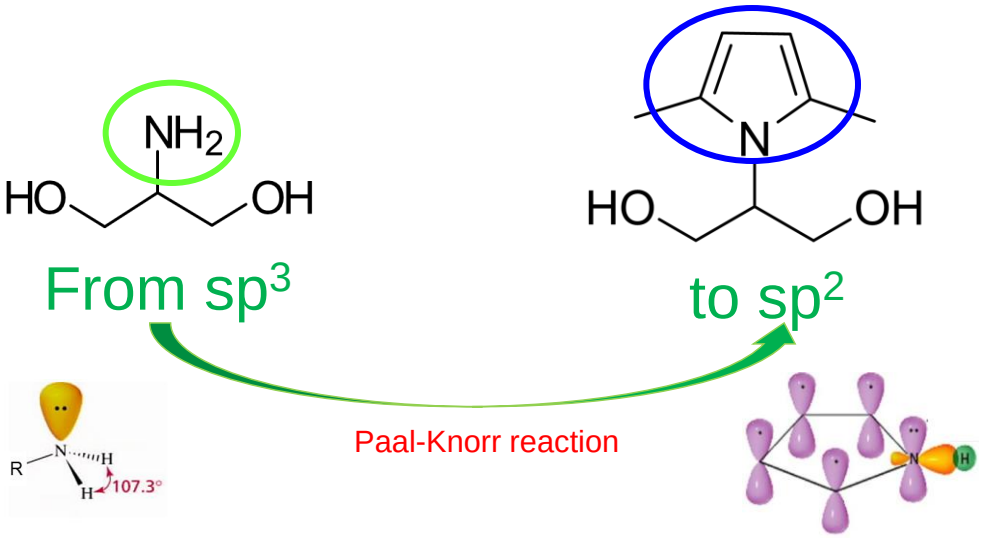
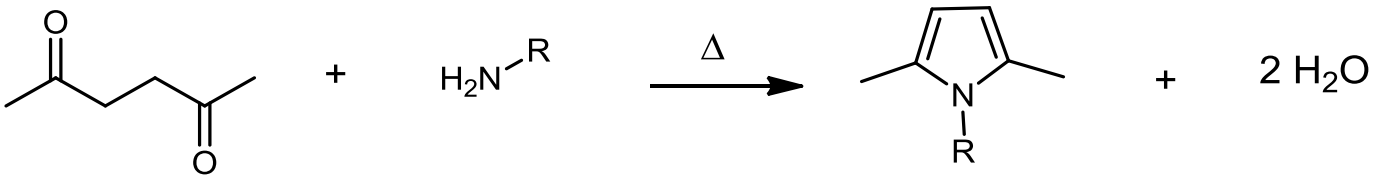
V. Barbera, S. Musto, A. Citterio, L. Conzatti, M. Galimberti,, *eXPRESS Polymer Letters* 2016, *10* (7) 548–558

Neat synthesis of Serinol pyrrole



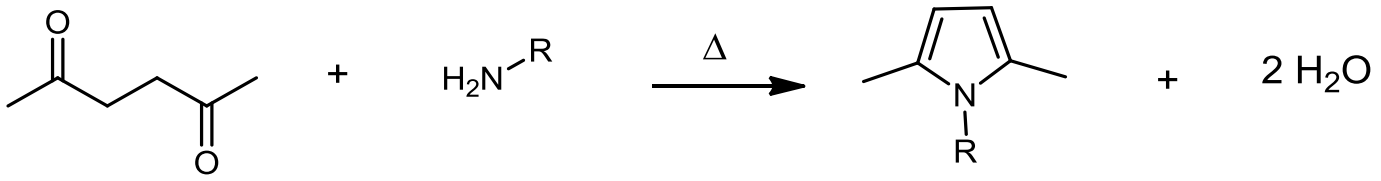
- Yield: at least 96%
- Atom efficiency: 85%
- Easy procedure
- No solvent
- By product: H_2O

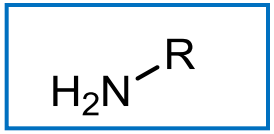
Pyrrole compounds (PyC) from neat Paal Knorr reaction

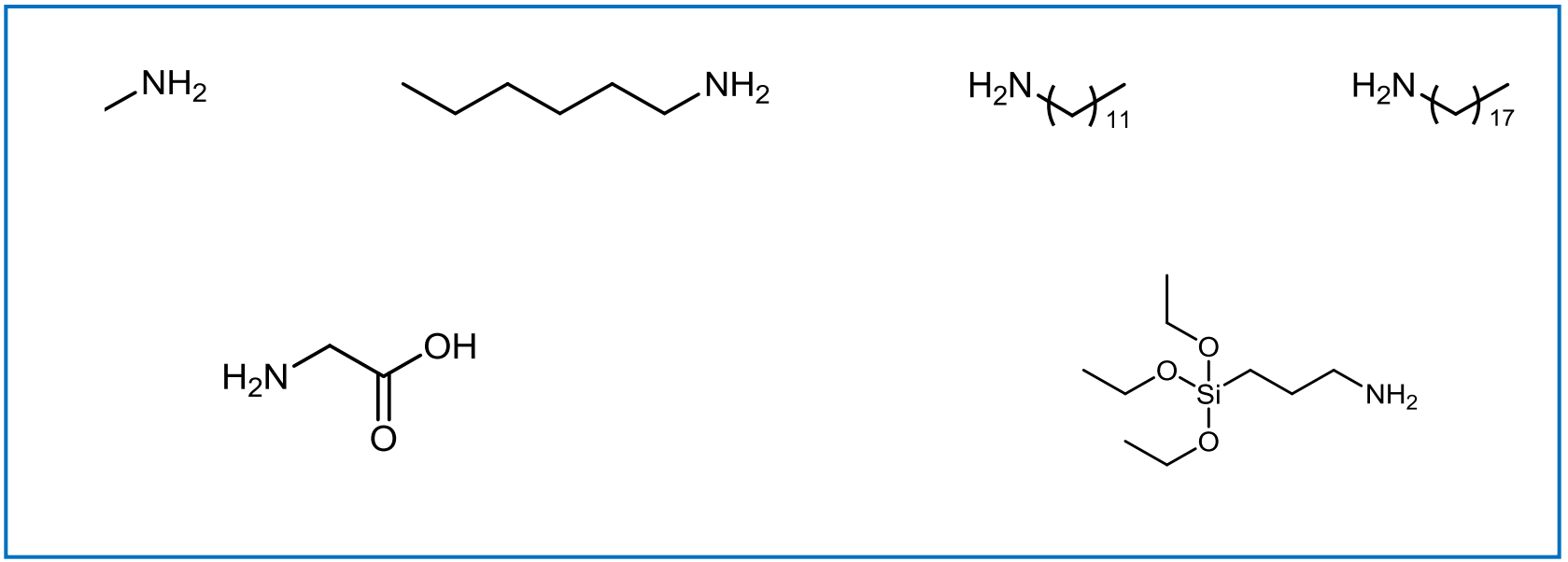


V. Barbera, A. Bernardi, A.Palazzolo, A. Rosengart, L. Brambilla, M. Galimberti Pure and Applied Chemistry 2018, 90(2), 253–270

Pyrrole compounds (PyC) from neat Paal Knorr reaction







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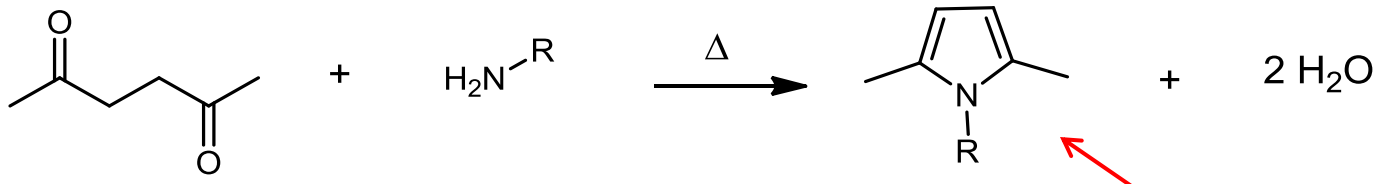
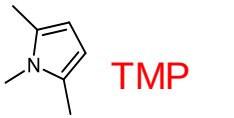


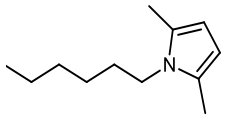
Same reaction conditions used for SP

PyC

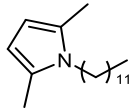
Yield %


TMP

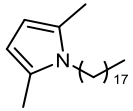
82


EP

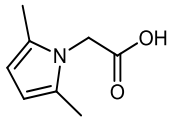
90


DDcP

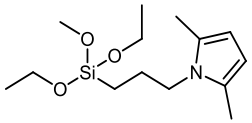
86


ODcP

88

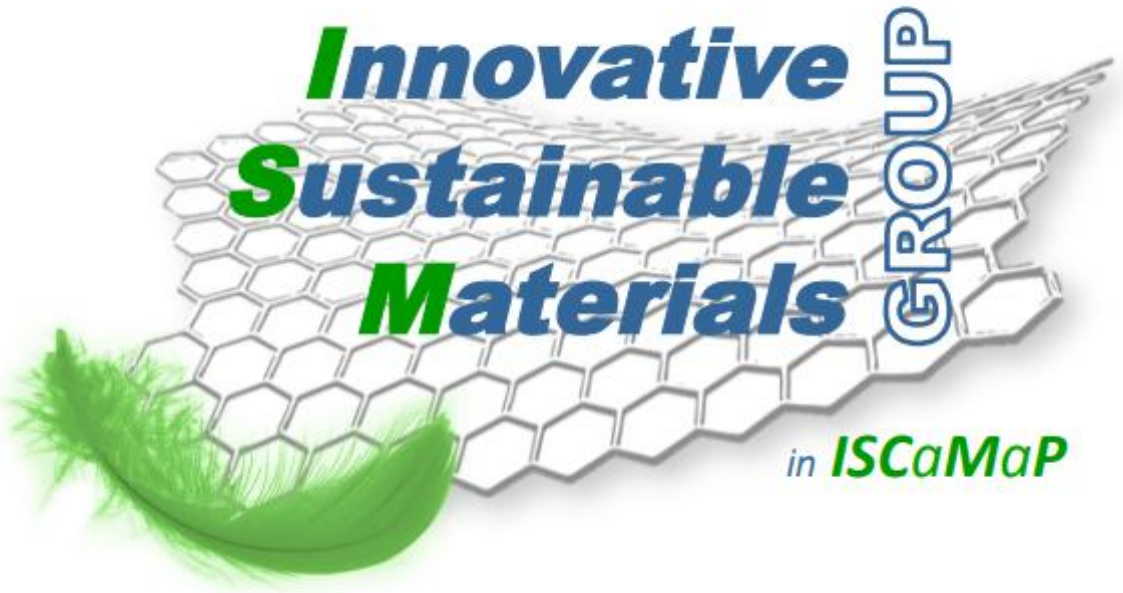

GlyP

85


APTESP

82

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



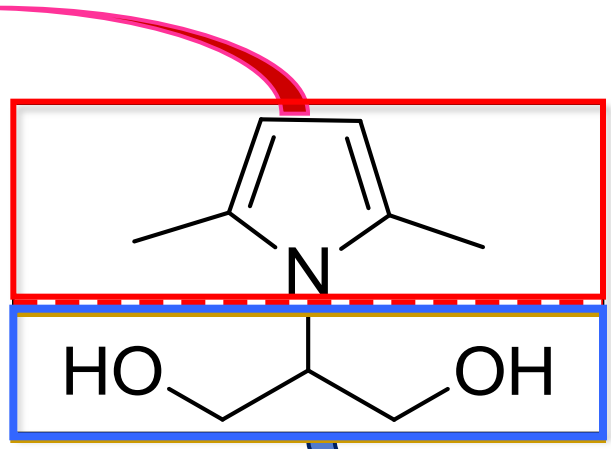
Janus molecules

for the functionalization of graphene layers

Serinolpyrrole: *Janus* molecule

INTERACTION
WITH
LIPOPHILIC MATRIX
AND
GRAPHITIC CARBONS.

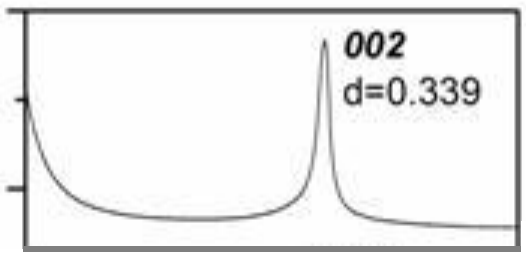
CHEMICAL REACTIVITY

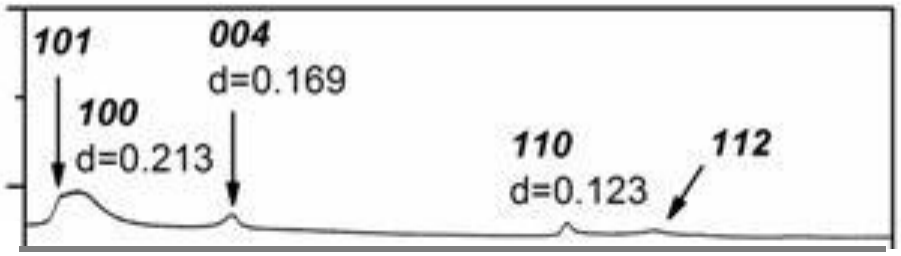


REACTIONS
WITH
FUNCTIONAL GROUPS

INTERACTION
WITH
DIFFERENT
SURROUNDING

High Surface Area Graphite (HSAG)



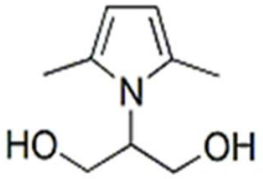


Sample	Surface area (m^2/g)	number of stacked layers	$D_{\parallel} / D_{\perp}$
HSAG	330	35	3.1

M. Mauro, V. Cipolletti, M. Galimberti, P. Longo, G. Guerra, *J.* Phys. Chem. C 116 (2012) 24809−24813

M. Galimberti, V. Cipolletti, S. Musto, S. Cioppa, G. Peli, M. Mauro, G. Guerra, S.Agnelli, T. Riccò, V. Kumar RCT (2014) 87(3) 417-442

HSAG-SP Adducts - Preparation



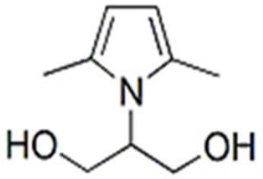
HSAG + SP

SP = 1 – 20 phc

phc = per hundred carbon

M. Galimberti, V. Barbera, S. Guerra, L. Conzatti, C. Castiglioni, L. Brambilla, A. RSC Adv., 2015, 5, 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.

HSAG-SP Adducts - Preparation



Mechanical treatment

Ball Milling:

300 rpm, 6h

HSAG + SP → HSAG/SP-M

SP = 1 – 20 phc

phc = per hundred carbon

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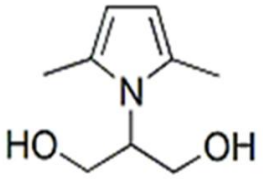
Galimberti M., Barbera V., Guerra S., Bernardi A., Rubber Chemistry and Technology, 2017, 90(2), 285-307.

HSAG-SP Adducts - Preparation



Mechanical treatment

Ball Milling:

300 rpm, 6h

HSAG + SP

SP = 1 – 20 phc

phc = per hundred carbon

HSAG/SP-M

80 - 180 C

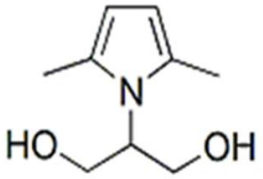
0,5 - 4 h

HSAG/SP-T

Thermal treatment

M. Galimberti, V. Barbera, S. Guerra, L. Conzatti, C. Castiglioni, L. Brambilla, A. RSC Adv., 2015, 5, 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.

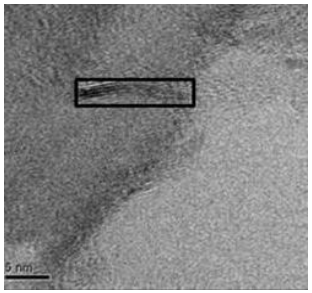
CA-SP Adducts - Yield of functionalization*



Thermal treatment

SP = 5 phc; 150°C, 2 h

HSAG



BET Surface area: [m^2/g] 300

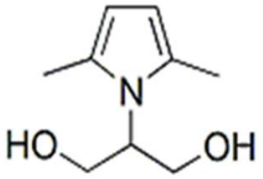
Functionalization Yield(%)*: 96

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

from TGA

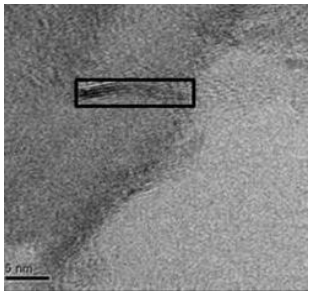
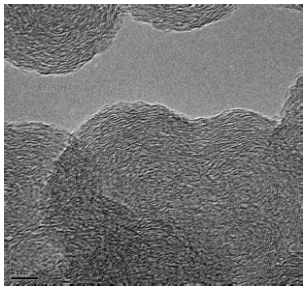
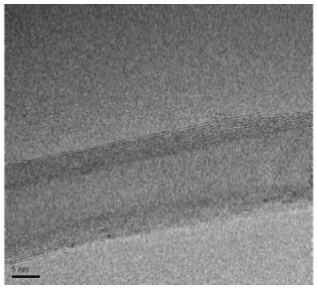
HSAG from Asbury

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

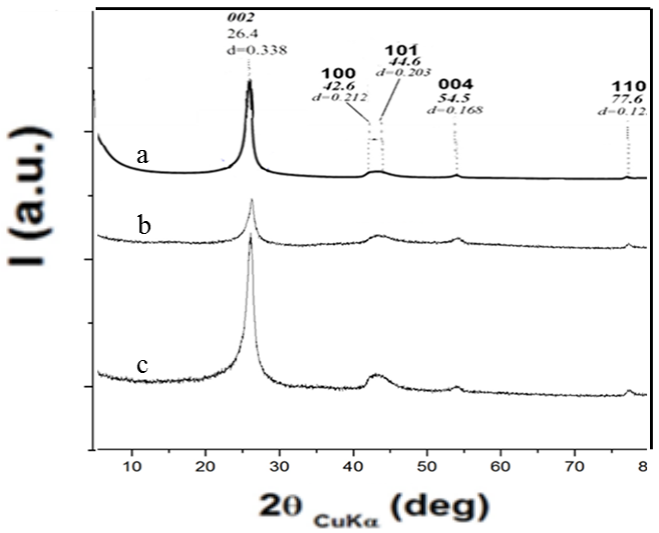
* $\text{Functionalization Yield (\%)} = 100 * \frac{\text{SP mass \% in (CA–SP adduct) after acetone washing}}{\text{SP mass \% in (CA–SP adduct) before acetone washing}}$ from TGA

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

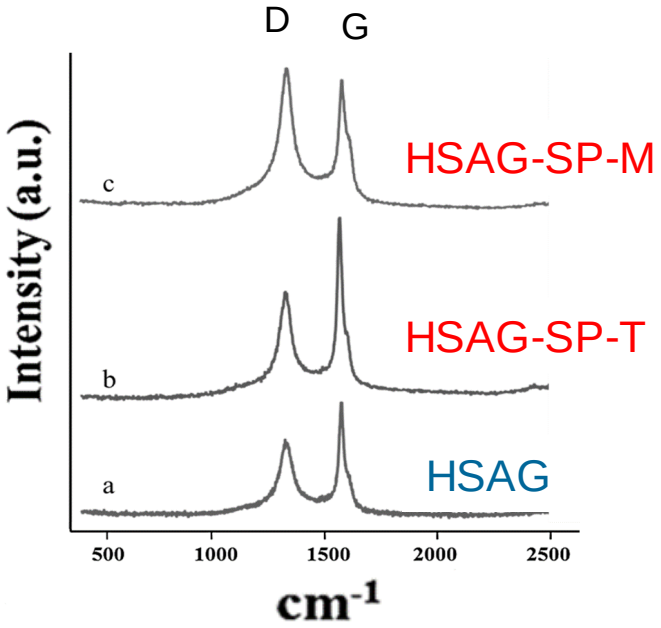


HSAG

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

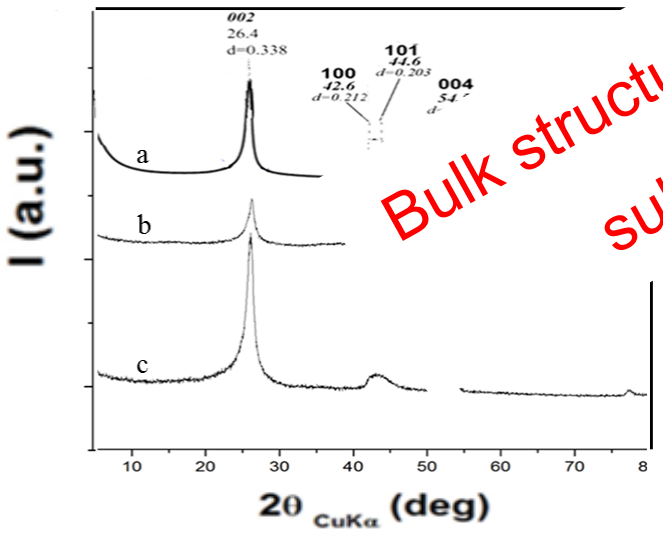
Galimberti M., Barbera V., Guerra S., Bernardi A., Rubber Chemistry and Technology, 2017, 90(2), 285-307.

Adducts of SP with high surface area graphite (HSAG)

CA/SP-T → Soxhlet extraction in ac[illegible]ne

Bulk structure of graphitic substrate substantially unaltered

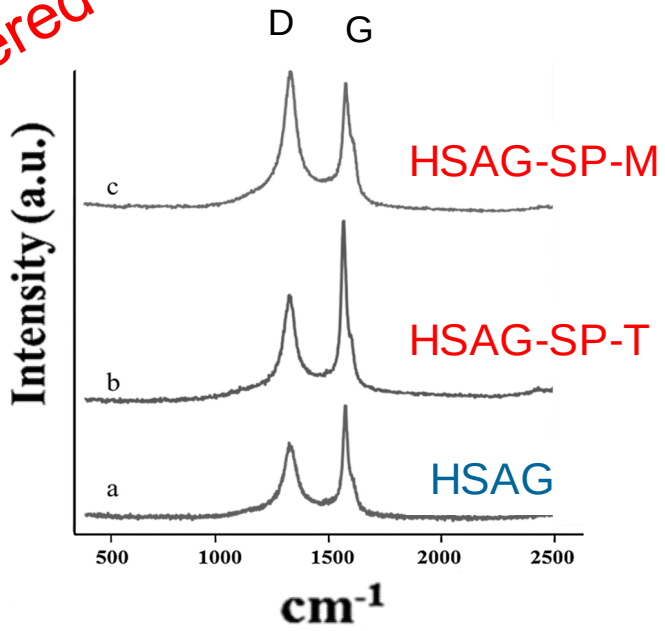
WAXD



HSAG-SP-M

HSAG-SP-T

Raman



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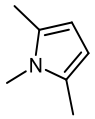
HSAG / PyC adducts

Functionalization Yield %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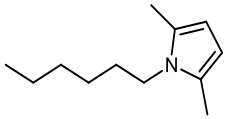
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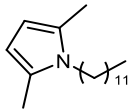
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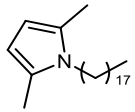
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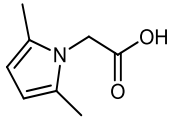
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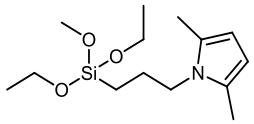
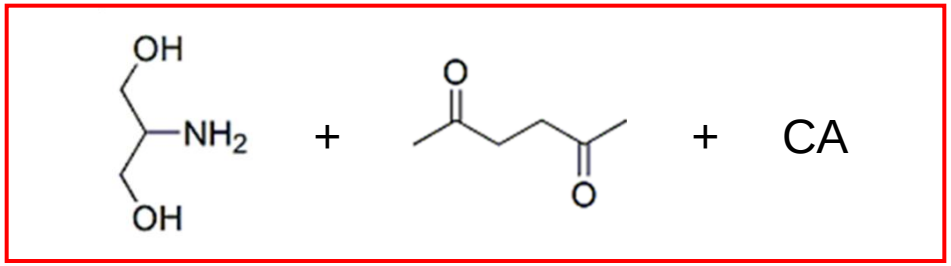

78

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

CA-SP Adducts - SP formed *in situ*

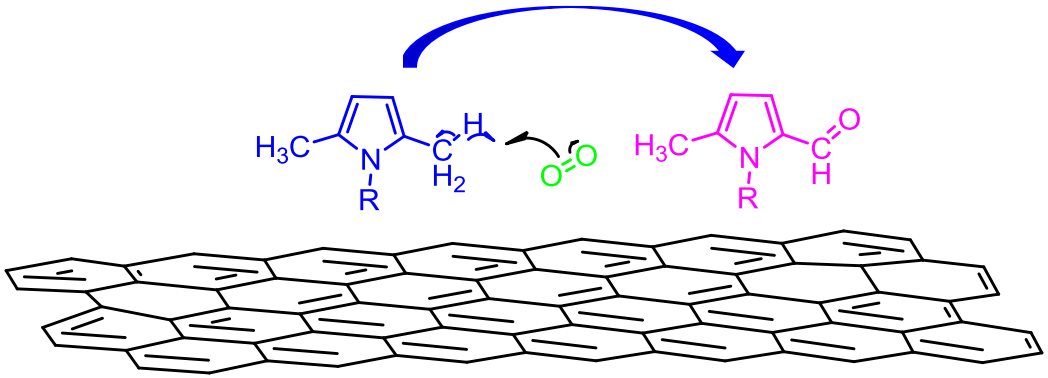


CA + SP

CA-SP adduct

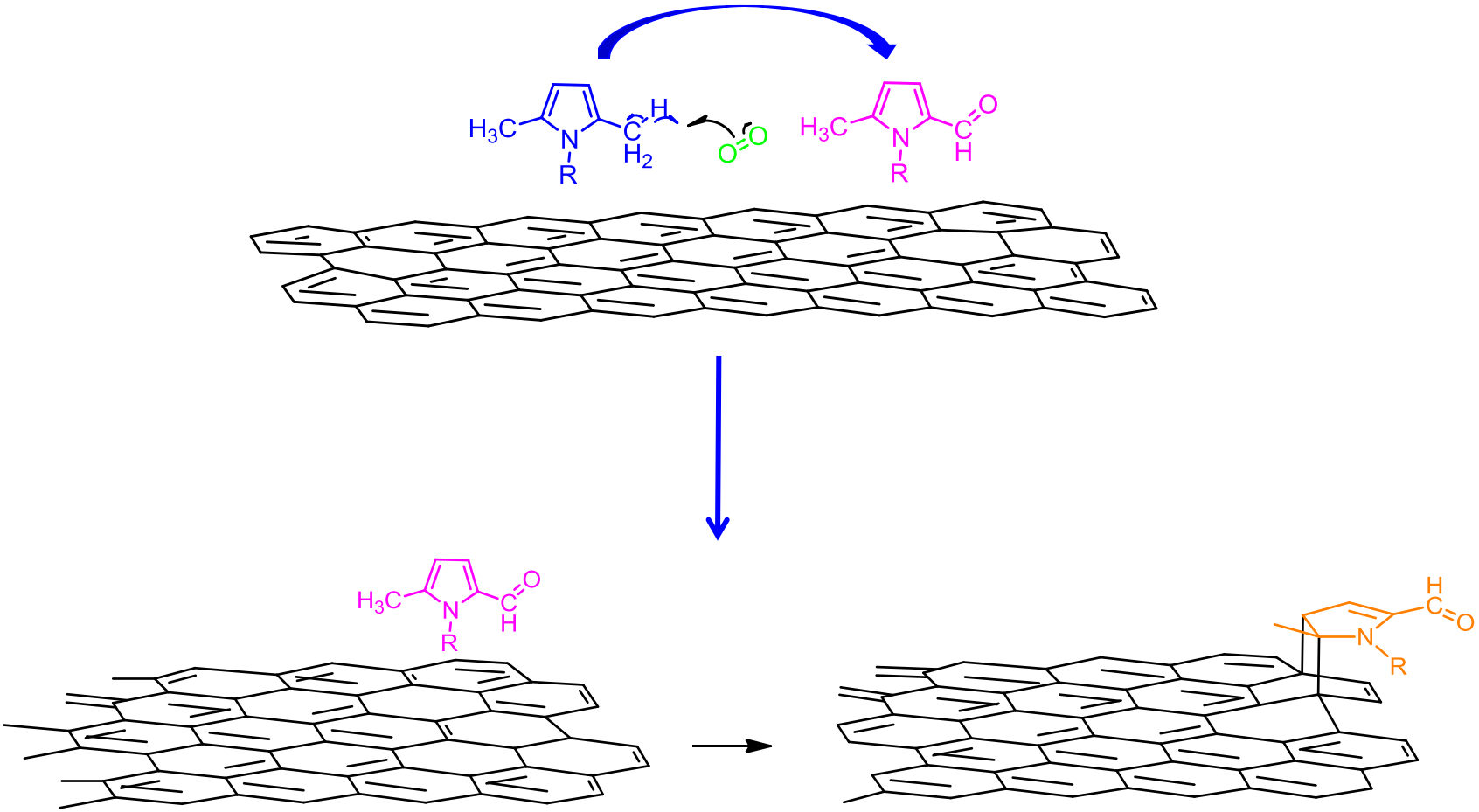
Mechanism of the functionalization reaction

TMP oxidation product - Reaction with a model substrate



Barbera, V., Brambilla, L., Milani, A., Palazzolo, A., Castiglioni, C., Vitale, A., Bongiovanni R., Galimberti, M. (2019). Nanomaterials, 9(1), 44.,

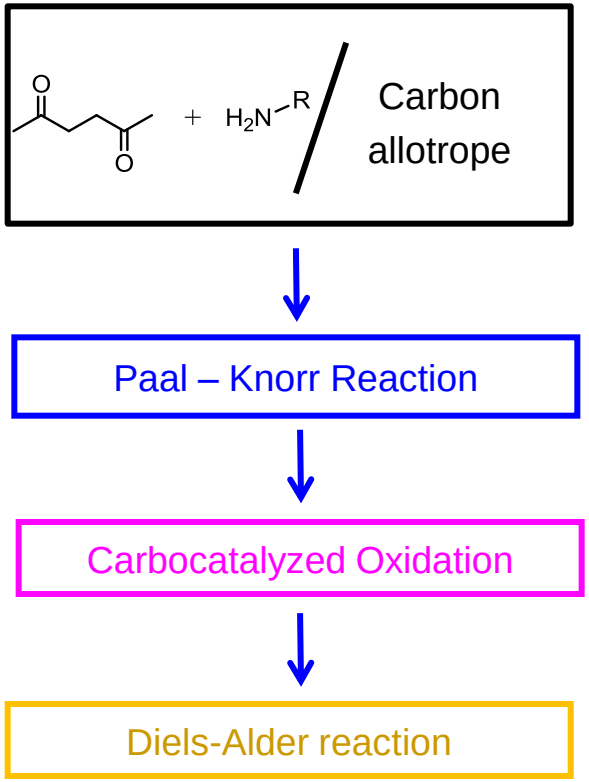
TMP oxidation product - Reaction with a model substrate

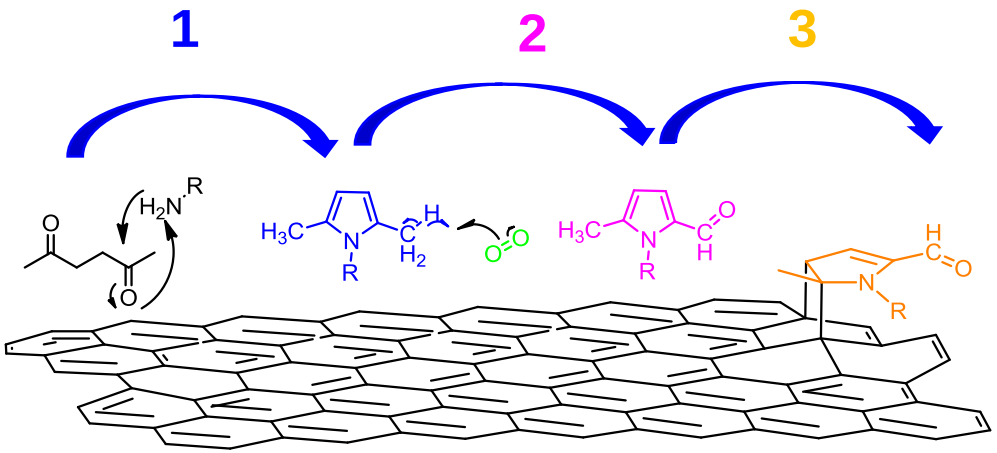


Barbera, V., Brambilla, L., Milani, A., Palazzolo, A., Castiglioni, C., Vitale, A., Bongiovanni R., Galimberti, M. (2019). Nanomaterials, 9(1), 44.,

Facile functionalization of carbon materials

Hypothesis for the mechanism





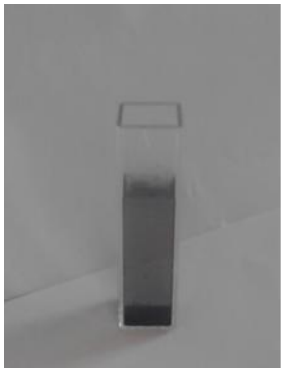
Barbera, V., Brambilla, L., Milani, A., Palazzolo, A., Castiglioni, C., Vitale, A., Bongiovanni R., Galimberti, M. (2019). Nanomaterials, 9(1), 44.,

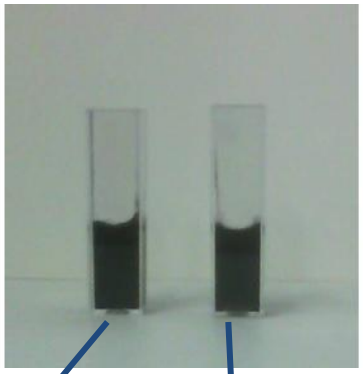
Tuning of solubility parameters

Water dispersions of HSAG-SP adducts

HSAG

HSAG-M

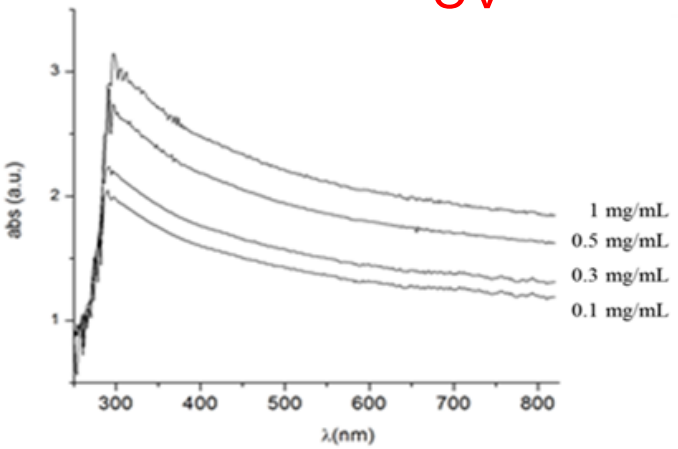


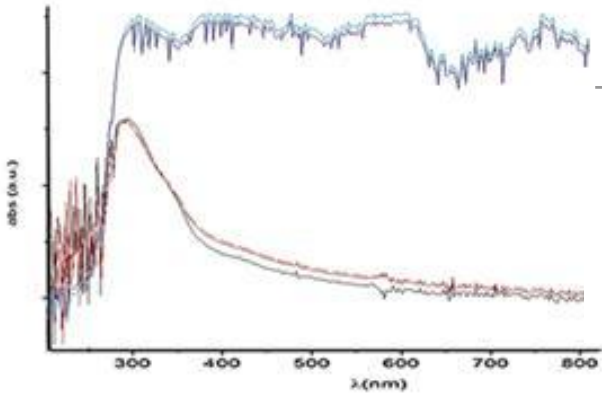


freshly prepared

after 30 min centrifugation
at 2000 rpm

UV





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

CA / PyC adducts - Tuning of solubility parameters

Experimental determination

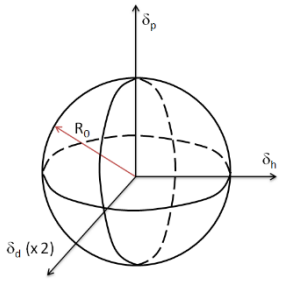
↓

Stable suspensions
in solvents
with different δ

Theoretical predictions

↓

Computational model:
Hansen solubility parameters

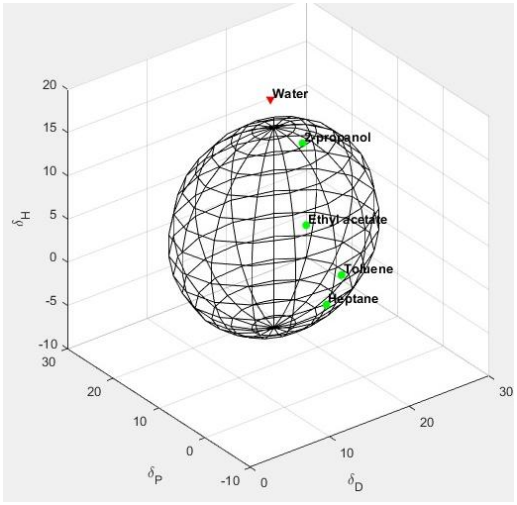


Solvents

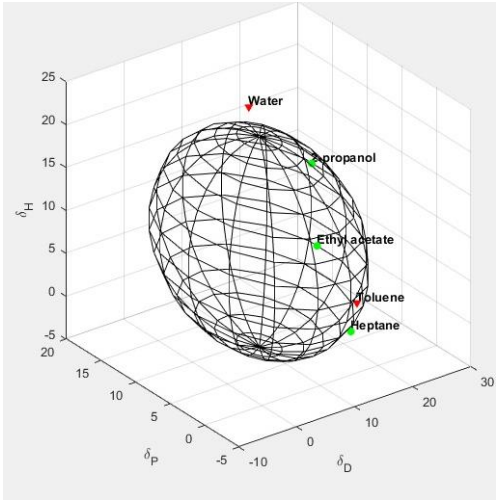
Hexane, Heptane, Cyclohexane, Toluene, Xylene, Chloroform, Ethyl acetate, Acetone, 2-propanol, Methanol, H_2O

Evaluation of solubility parameters of HSAG-PyC - Hansen sphere

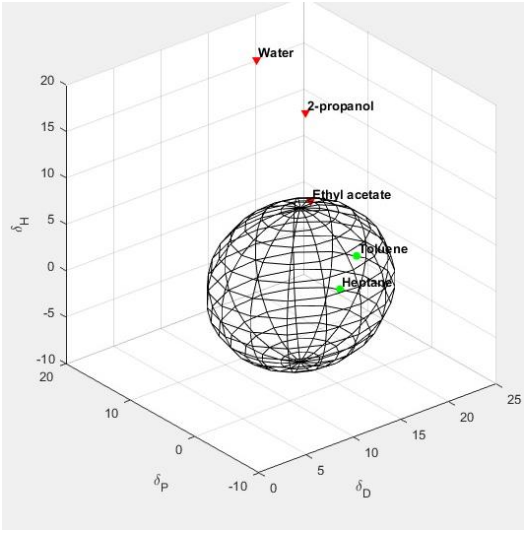
HSAG-TMP



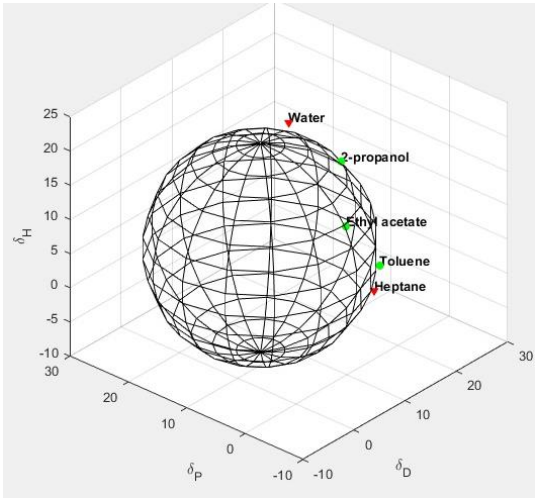
HSAG-DDcP



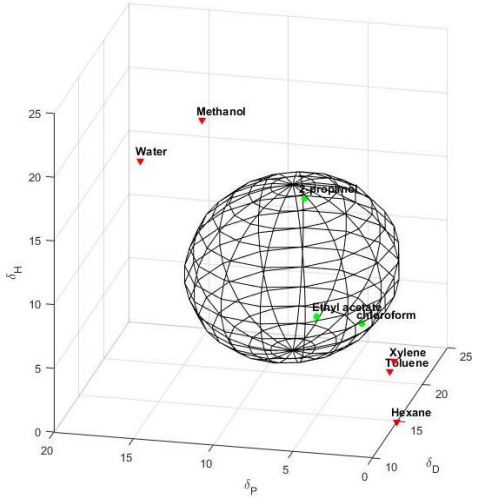
HSAG-APTESP

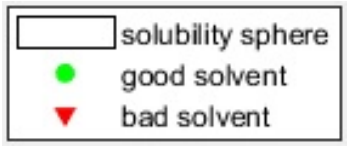


HSAG-GlyP



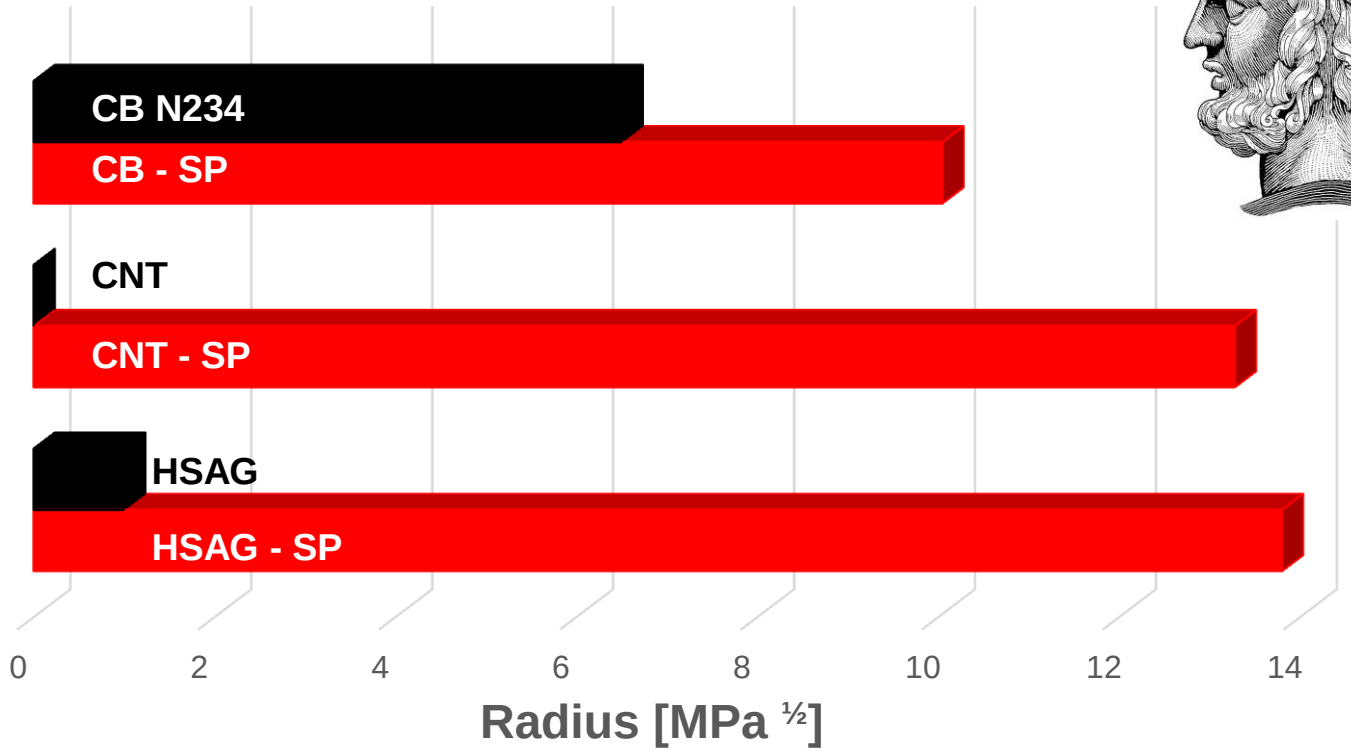
HSAG-SP



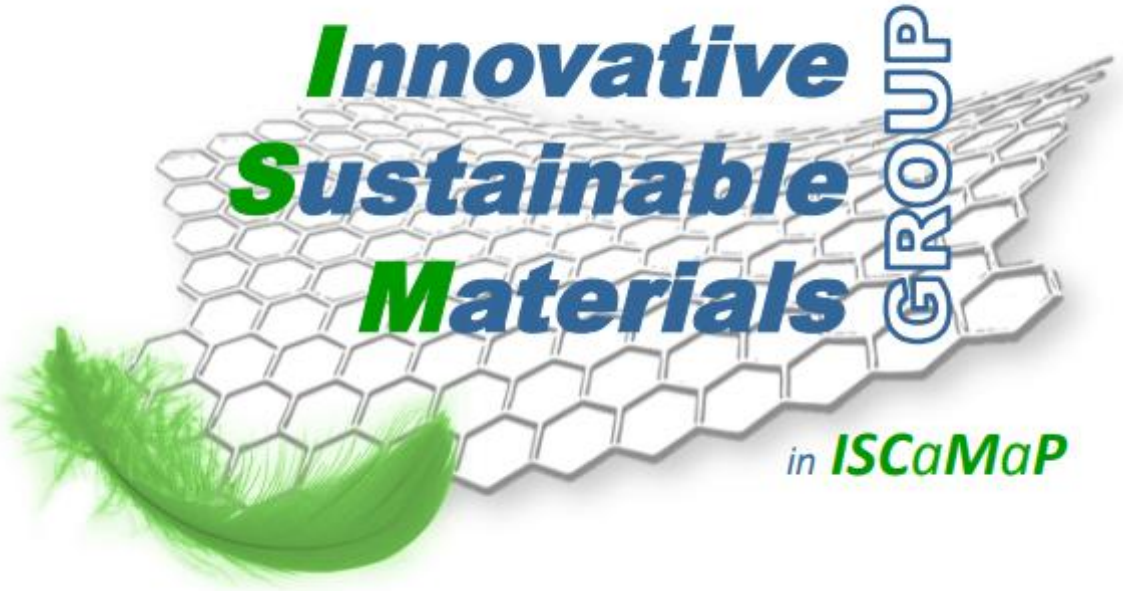


V. Barbera, A. Bernardi, A.Palazzolo, A. Rosengart, L. Brambilla, M. Galimberti Pure and Applied Chemistry 2018, 90(2), 253–270

Evaluation of solubility parameters of CA-SP - Radius comparison



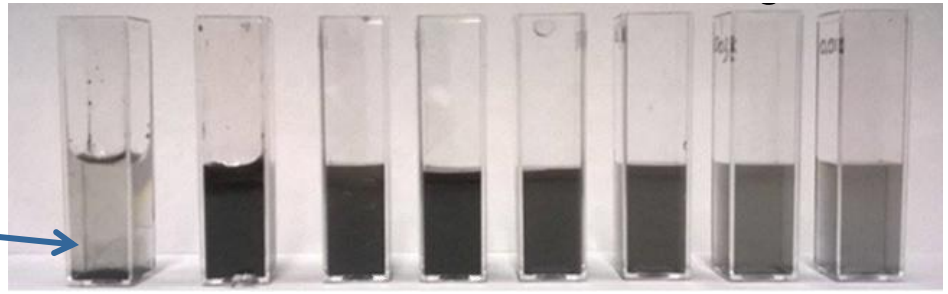
(*) Amount of SP on CA: 10 mass%



Applications

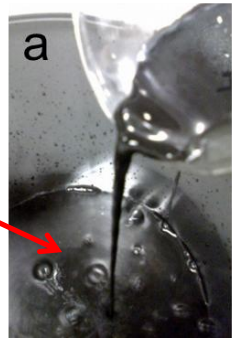
Inks and varnishes

without SP



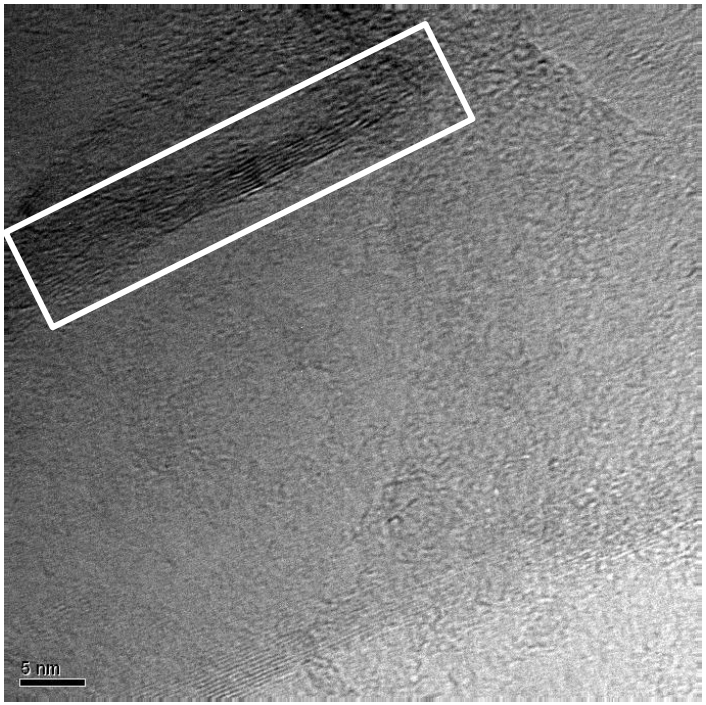
Conc (g/L): 10 5.0 2.5 1.0 0.50 0.25 0.10

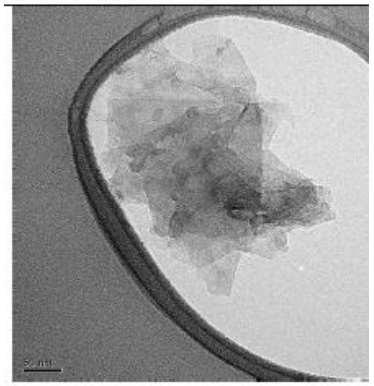
Large scale preparation



Conc (g/L): 10 g/L, 30 g/L 200 g/L.

Water based few layers graphene





HR-TEM micrographs

From 8 – 10 layers to few layers graphene

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

Composites from water dispersions of HSAG-SP adducts

Aerogels

Polymer: carboxymethylcellulose

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

V. Barbera, S. Guerra, L. Brambilla, M. Maggio, A. Serafini, L. Conzatti, A. Vitale, M. Galimberti, Biomacromolecules, 2017, 18 (12), 3978–399

Innovative step-growth polymers: polyurethanes

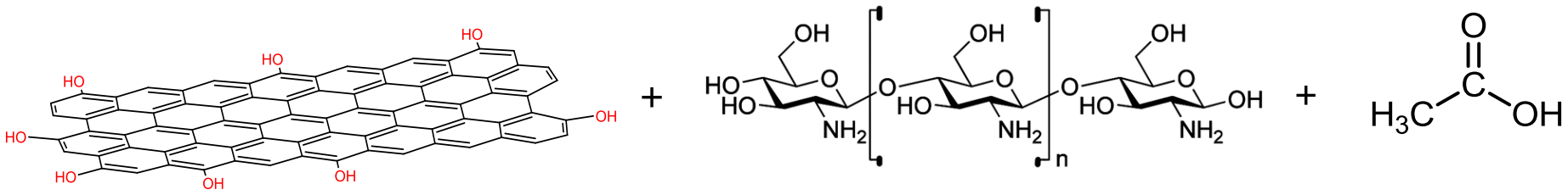
HSAG-SP

2% by mass in polyol

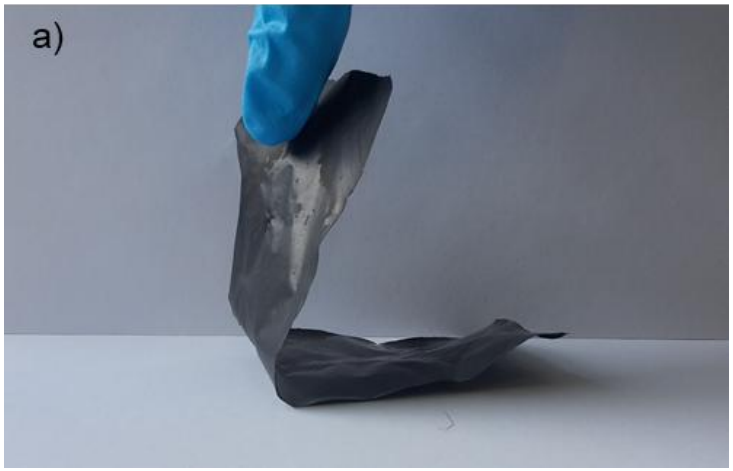
No HSAG HSAG HSAG-SP

Large scale preparation

Bio-based composite materials



Water
Room temperature



Carbon paper

Aerogels

V. Barbera, S. Guerra, L. Brambilla, M. Maggio, A. Serafini, L. Conzatti, A. Vitale, M. Galimberti, Biomacromolecules, 2017, 18 (12), 3978–399

NanoCarbon Up Technology

10 families of patents

Patents for this presentation

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

M. Galimberti, V. Barbera, R. Sebastiano, A. Truscello, A.M. Valerio.
EP 3180379 B1

M. Galimberti, V. Barbera, R. Sebastiano, A. Citterio, G. Leonardi, A.M. Valerio.
EP 3209604 B1; US10160652 B2

M. Galimberti, V. Barbera
PCT/IB2017/057001

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World Innovation
Conference & Expo

Thanks for the Attention!

Innovative Sustainable Materials GROUP
in ISCaMaP

instagram: @ismaterials.polimi

NR/HSAG composites - Electrical conductivity

NR latex dispersion of HSAG

↓

Addition of vulcanizers via melt blending

↓

Vulcanization

↓

Electrical conductivity

Electrical conductivity