From biosourced monomers to self assembly of graphene based catalysts

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MIPOL 2021 – Milan Polymer Days – July 6-8, 2021

Items of the presentation

- Biosourced *Janus* molecule
- The functionalization of sp^2 carbon allotropes
- Waterborne nanoreactors
- The nanoreactors for organic synthesis

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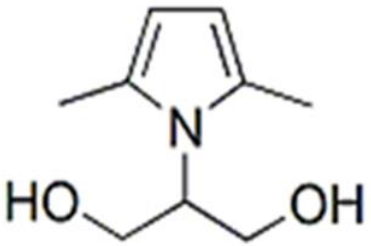
Lucia Rubino

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

Biosourced *Janus* molecule

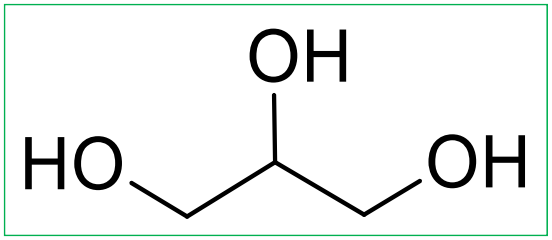
A biosourced *Janus* molecule



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

Serinol pyrrole - SP

A route for preparing serinol pyrrole. From glycerol



Propane-1,2,3-triol

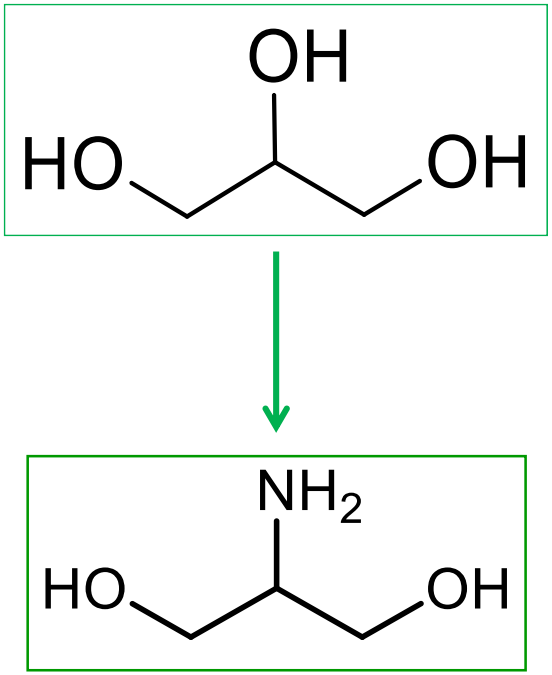
easily available, cheap raw material

main by-product of bio-diesel production

not toxic

biodegradable

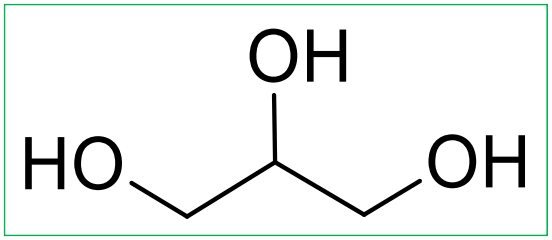
A route for preparing serinol pyrrole. From glycerol to serinol



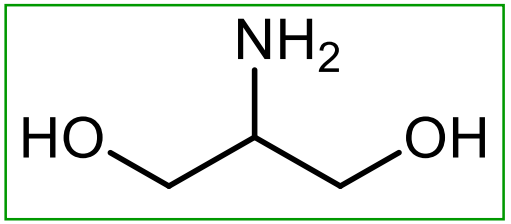
Propane-1,2,3-triol

2-Amino-1,3-propanediol

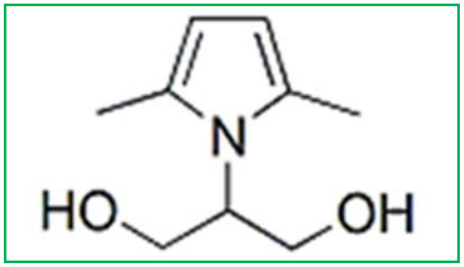
A route for preparing serinol pyrrole. From serinol to serinol pyrrole



Propane-1,2,3-triol

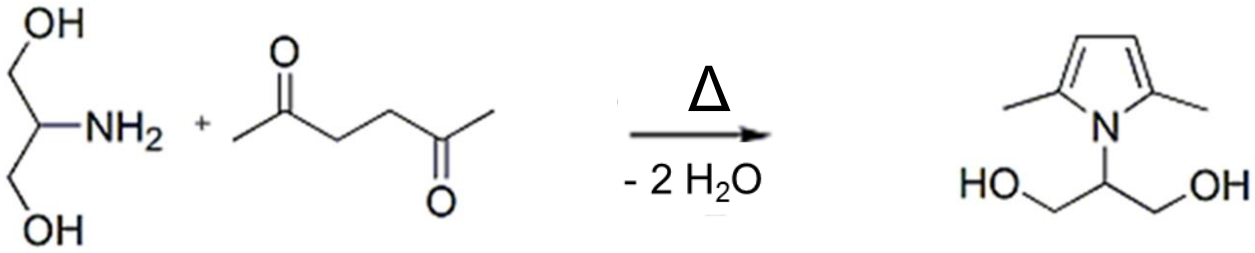


2-Amino-1,3-propanediol



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

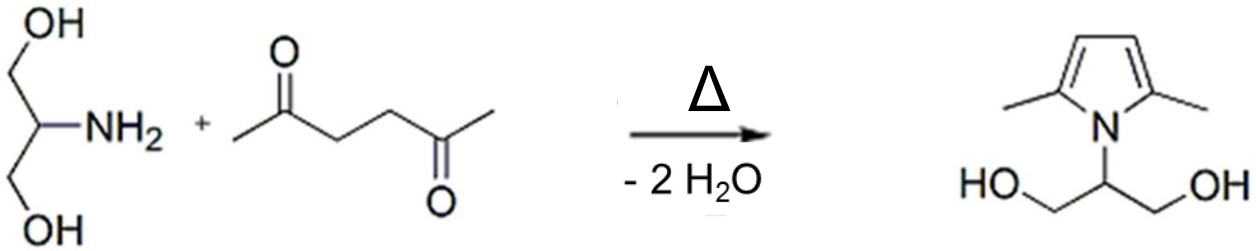
A route for preparing serinol pyrrole. From serinol to serinol pyrrole

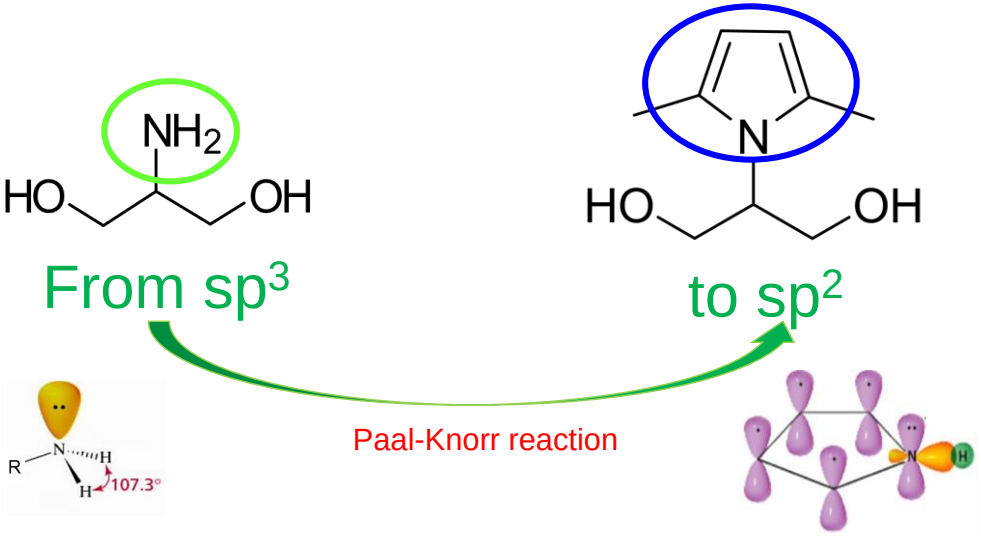


- Yield: at least 96%
- Atom efficiency: 85%
- Easy procedure
- No solvent
- By product: H_2O

US10329253 B2; EP3154939 B1. V. Barbera, A. Citterio, M. Galimberti, G. Leonardi, R. Sebastiano, S. U. Shisodia, A. M. Valerio

A route for preparing serinol pyrrole. From serinol to serinol pyrrole

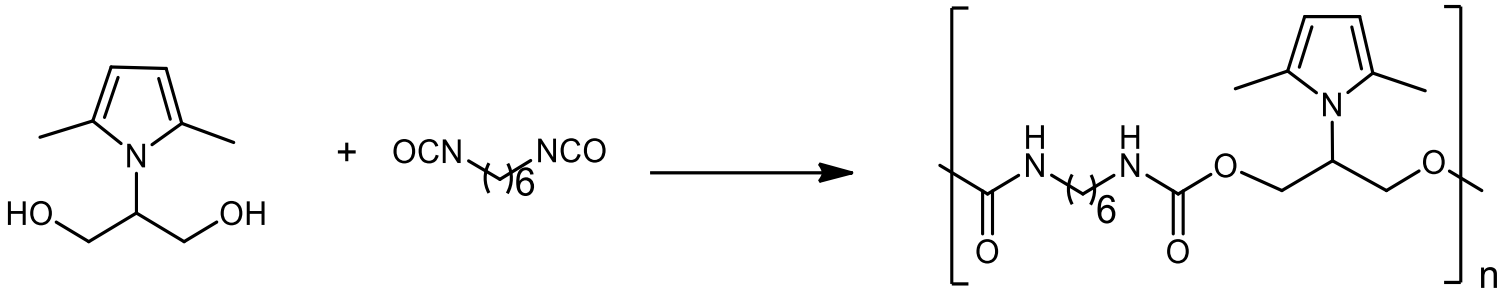




US10329253 B2; EP3154939 B1. V. Barbera, A. Citterio, M. Galimberti, G. Leonardi, R. Sebastiano, S. U. Shisodia, A. M. Valerio

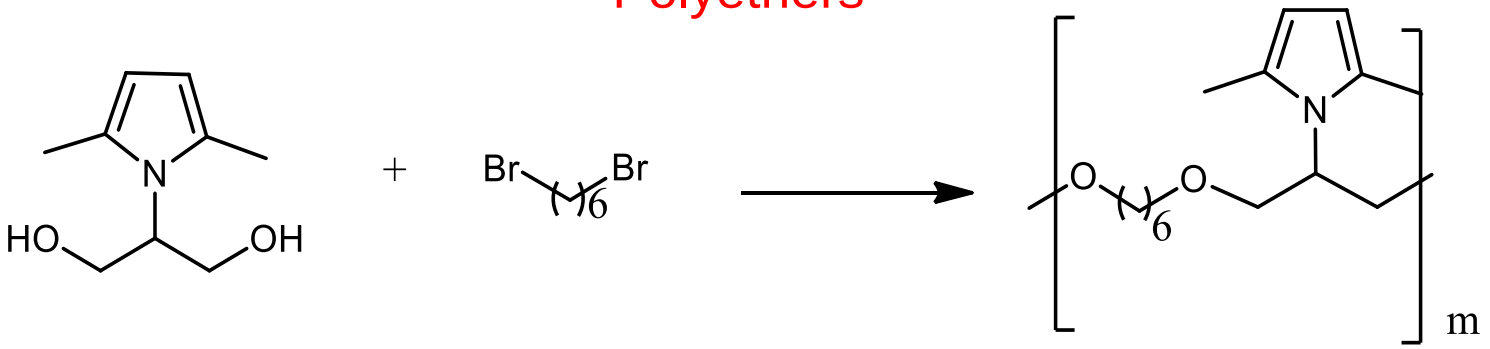
Stepgrowth polymers based on serinolpyrrole

Polyurethanes



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

Polyethers



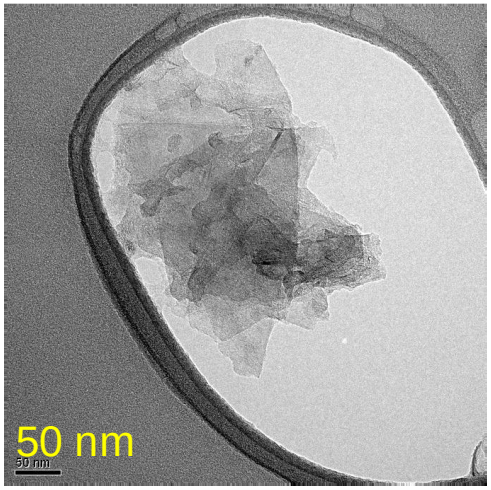
V. Barbera, S. Musto, A. Citterio, L. Conzatti, M. Galimberti, eXPRESS Polymer Letters 2016, 10 (7) 548–558

EP3180379 B1. M. Galimberti, V. Barbera, A. Truscello, R. Sebastiano, A. M. Valerio

The biosourced *Janus* molecule

and the functionalization of sp^2 carbon allotropes

The graphitic substrate: nanographite

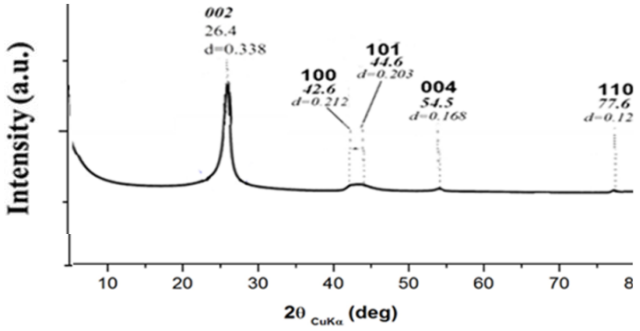


High surface area graphite (HSAG)

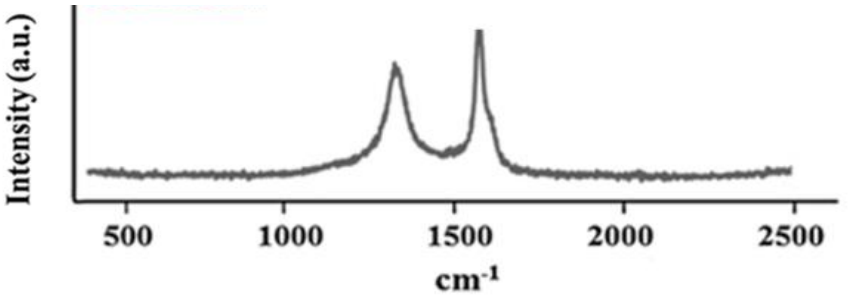
Surface area: 300 m2/g

Number of stacked layers: ca 35

WAXD



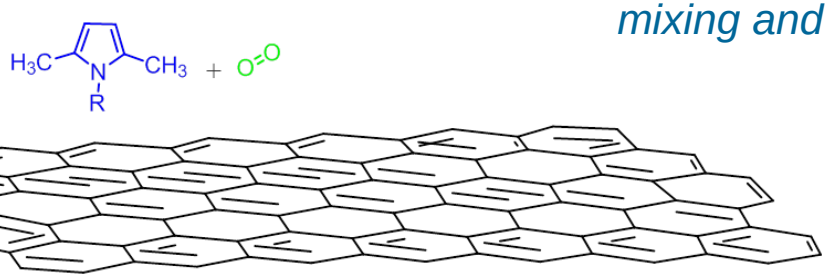
Raman



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

Reaction of the pyrrole compound with an sp^2 carbon allotrope

mixing and heating



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

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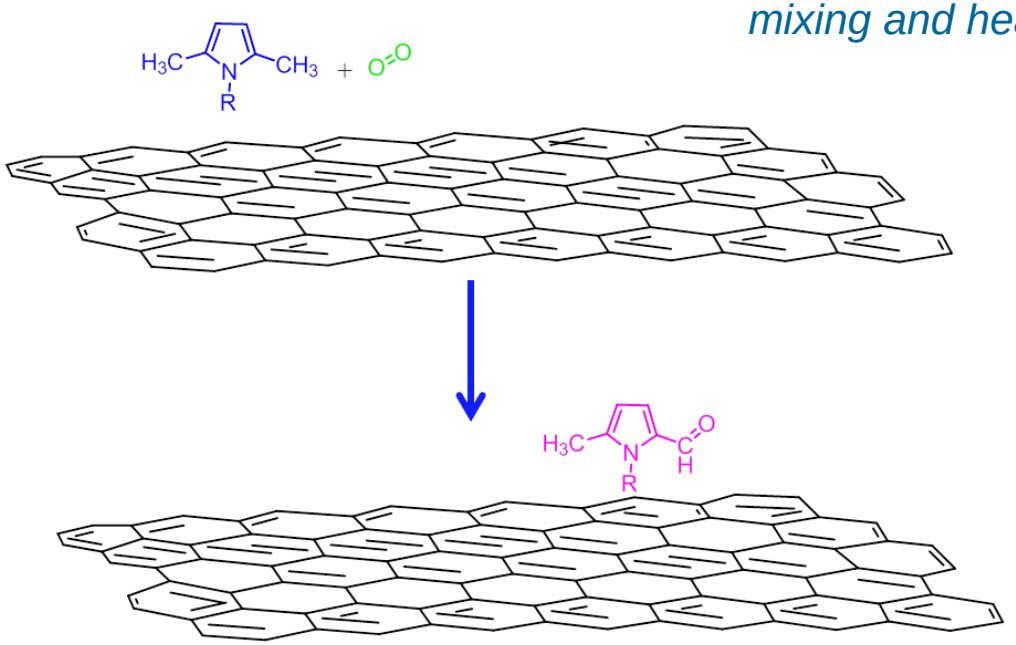

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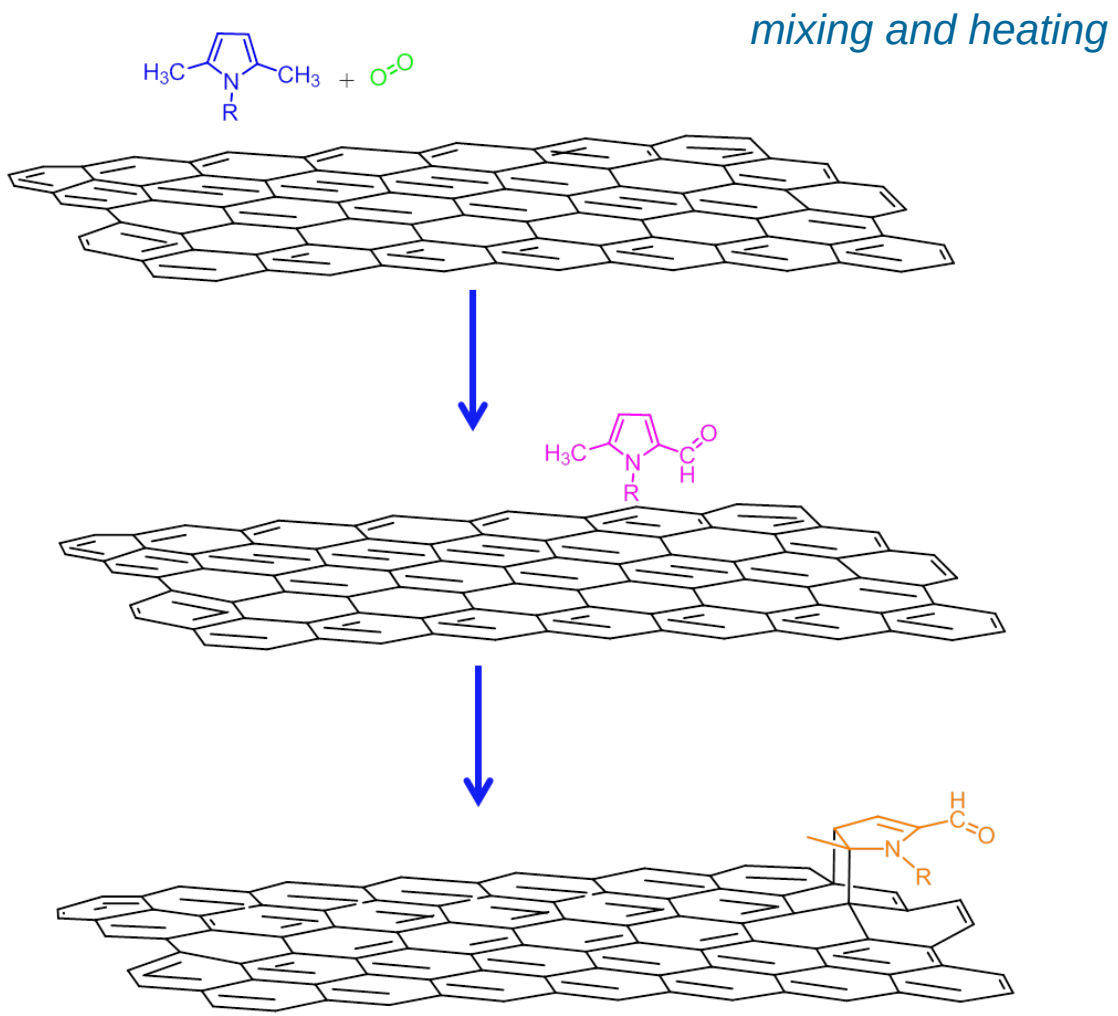
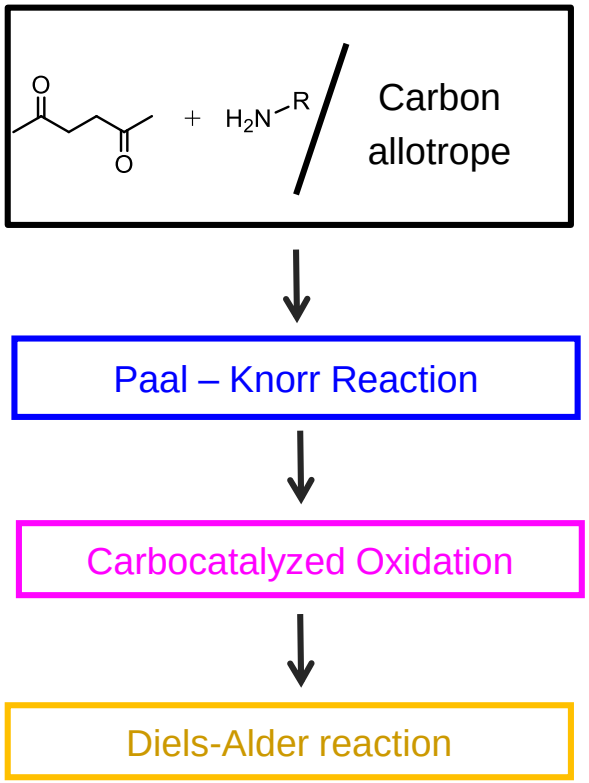
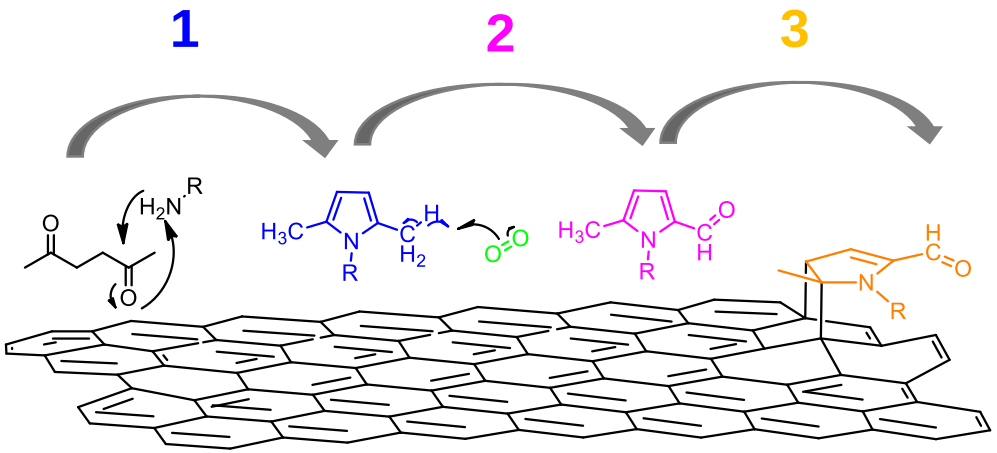


V. Barbera, L. Brambilla, M. Milani, A. Palazzolo, C. Castiglioni, A. Vitale, R. Bongiovanni, M. Galimberti, 2019. Nanomaterials, 9(1), p.44.

Reaction of the pyrrole compound with an sp^2 carbon allotrope

Domino reaction





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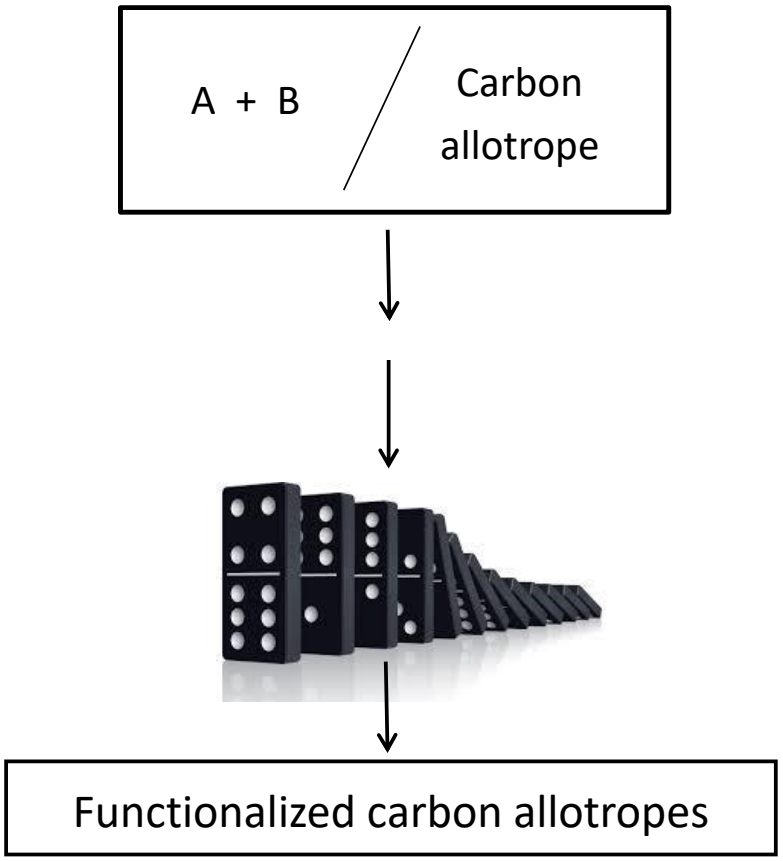
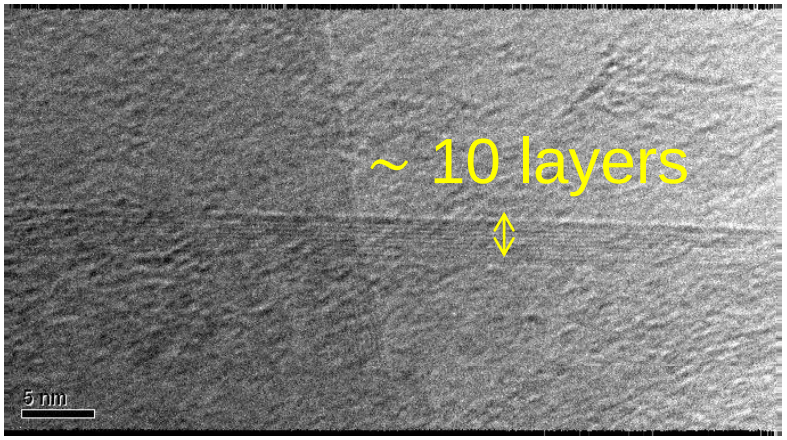
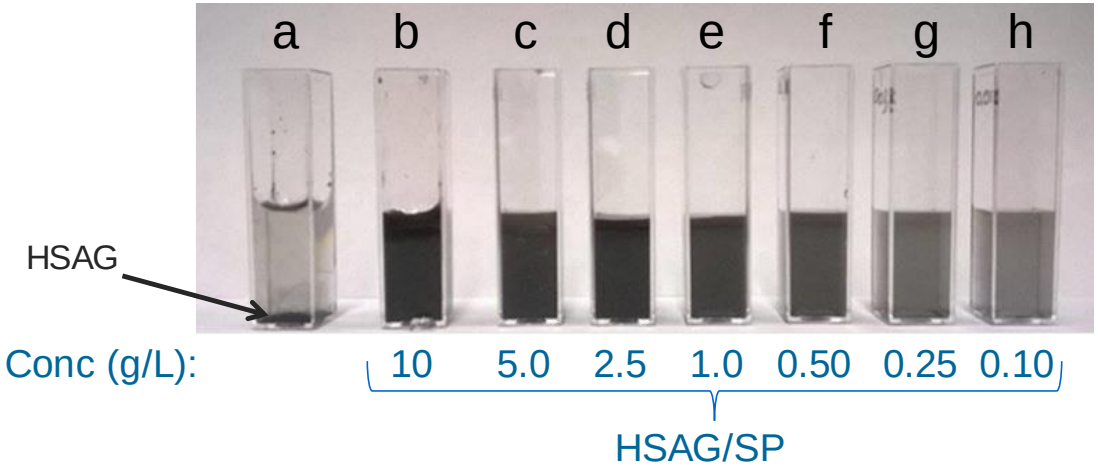


- Functional group:
  from few % to 20%
- Functionalization yield:
  from 85% to quantitative
- Covalent bond
  between functional group and carbon allotrope
- Bulk structure of graphitic materials:
  substantially unaltered

V. Barbera, A. Citterio, M. Galimberti, G. Leonardi, R. Sebastiano, S.U. Shisodia, A.M. Valerio. *US10329253B2*
M. Galimberti, V. Barbera, R. Sebastiano, A. Citterio, G. Leonardi, A.M. Valerio. *US10160652B2*
M. Galimberti, V. Barbera, R. Sebastiano, A. Truscello, A.M. Valerio. *EP3180379B1*
M. Galimberti, V. Barbera, *EP3538511A1*
M. Galimberti, V. Barbera, *EP3538481A1*

Production of few layers graphene





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

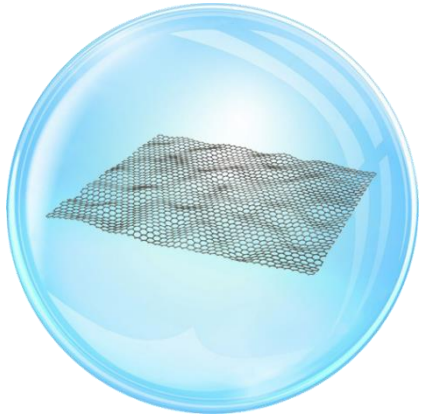
Graphene-based waterborne nanoreactors

for the confinement of organic synthesis

Waterborne nanoreactors based on graphene layers

Why graphene layers?

- ☞ High surface area
- ☞ π – electron density

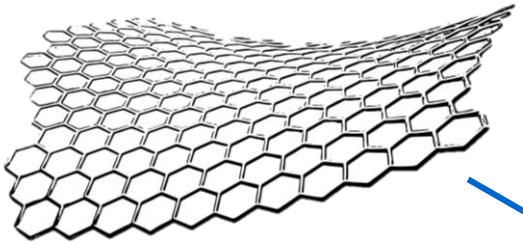


Why nanoreactors in water?

- ☞ To make reactions in confined space
- ☞ To improve the yields
- ☞ To avoid the use of toxic solvents
- ☞ To carry out more sustainable reactions

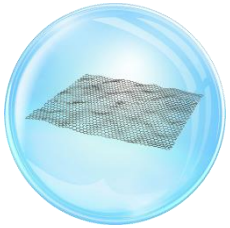
The Nanoreactor

Covalent functionalization with SP



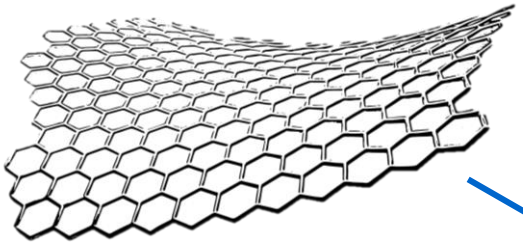
Supramolecular interaction with pyrrole containing polymeric surfactants

micelles



The Nanoreactor

Covalent functionalization with SP



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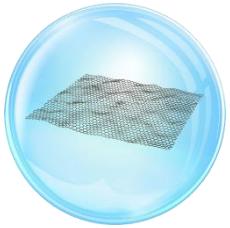
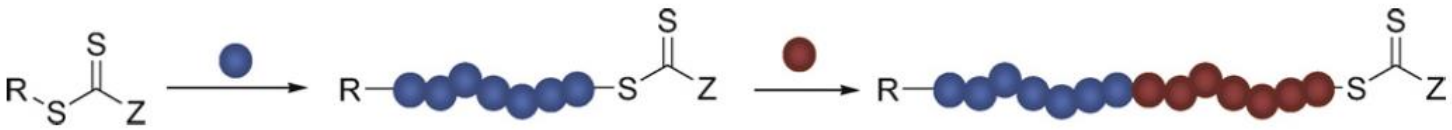


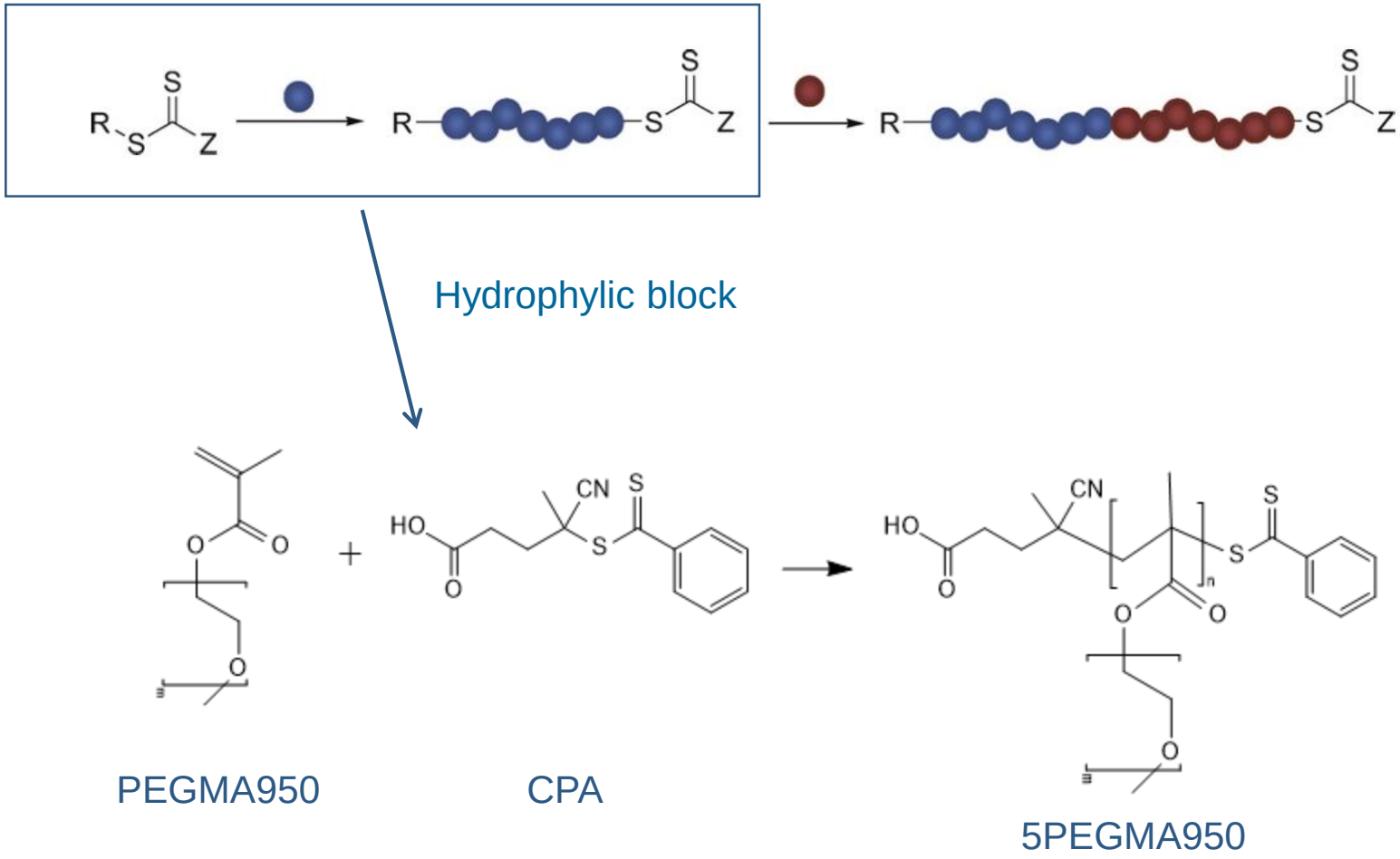
Lipophilic microenvironment and catalytic component

Confined space

Amphiphilic block copolymers via RAFT polymerization



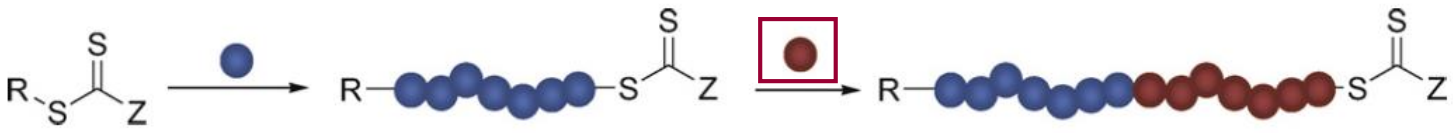
Amphiphilic block copolymers via RAFT polymerization



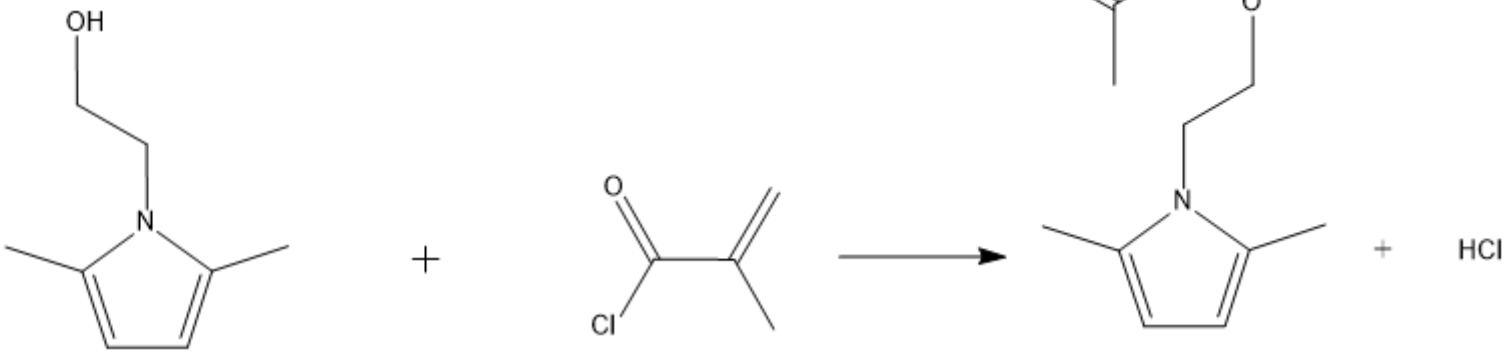
PEGMA950 = Poly(ethylene glycol)methyl ether methacrylate

CPA = 4-cyano-4 (phenylcarbonothioylthio)-pentanoic acid

Amphiphilic block copolymers via RAFT polymerization



The monomer for the lipophilic block



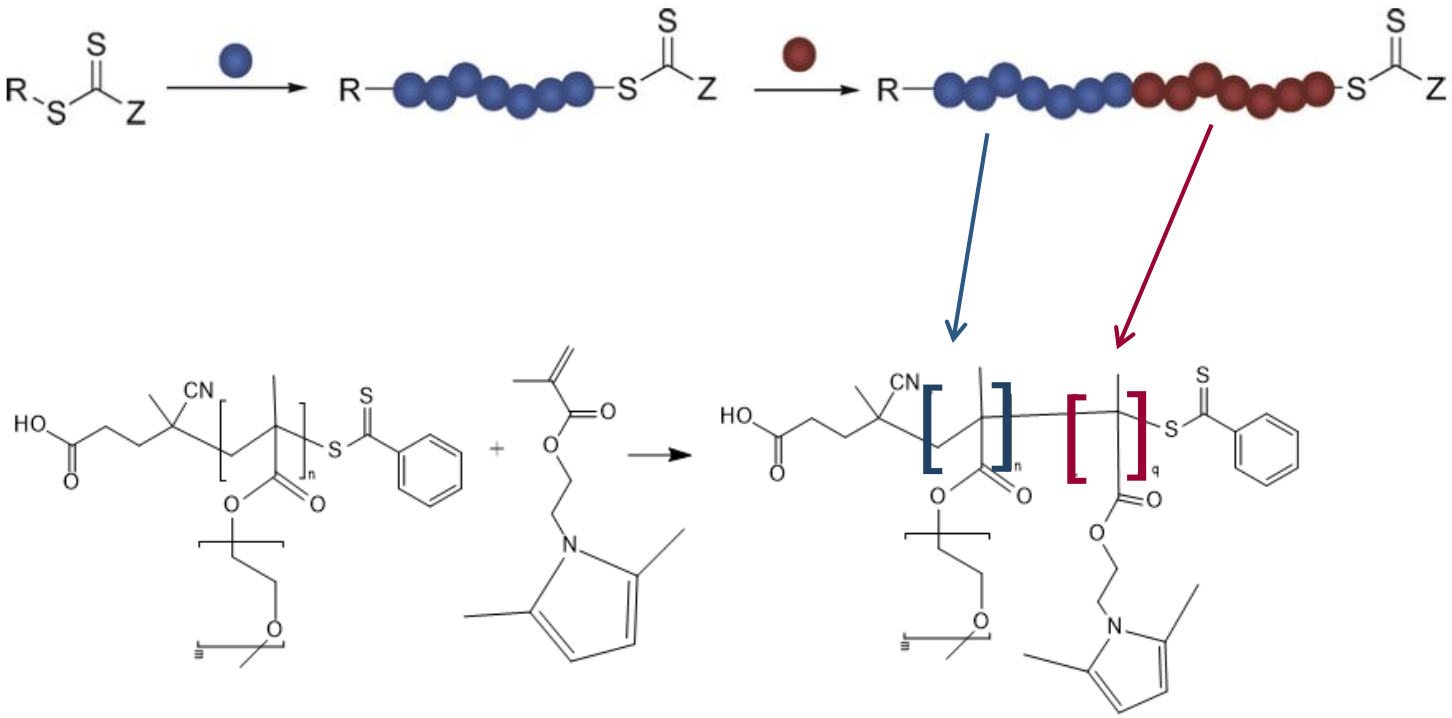
ethanol pyrrole (EP)

methacryloyl chloride

EPMA

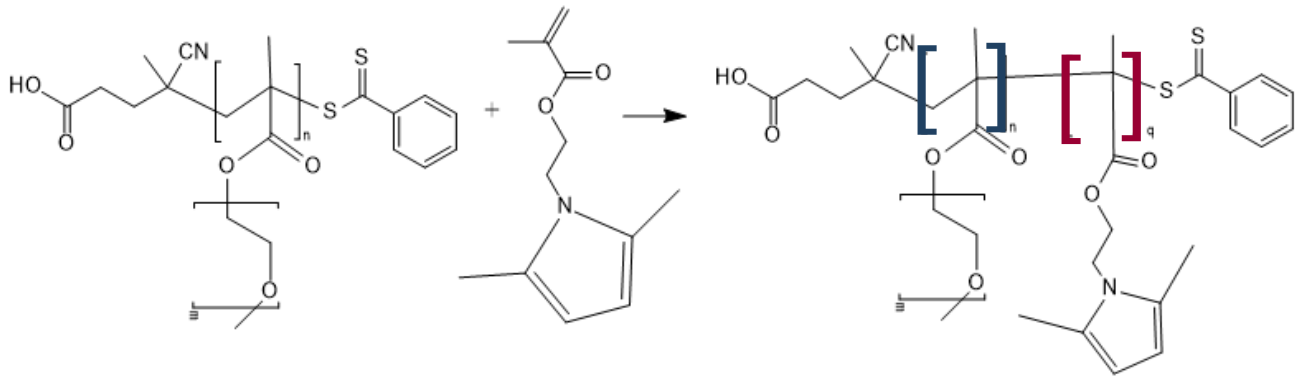
EPMA = 2-(2,5-dimethyl-1*H*-pyrrol-1-yl) ethyl methacrylate

Amphiphilic block copolymers via RAFT polymerization

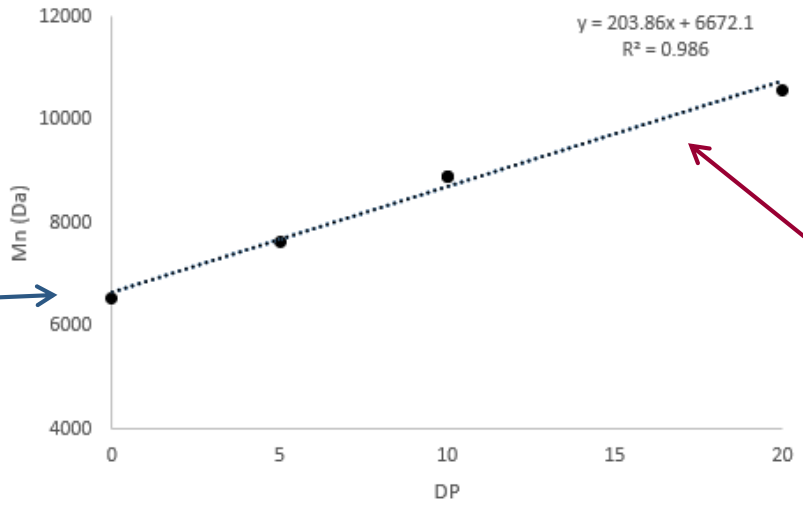


5PEGMA950-p(EPMA)

Amphiphilic block copolymers via RAFT polymerization



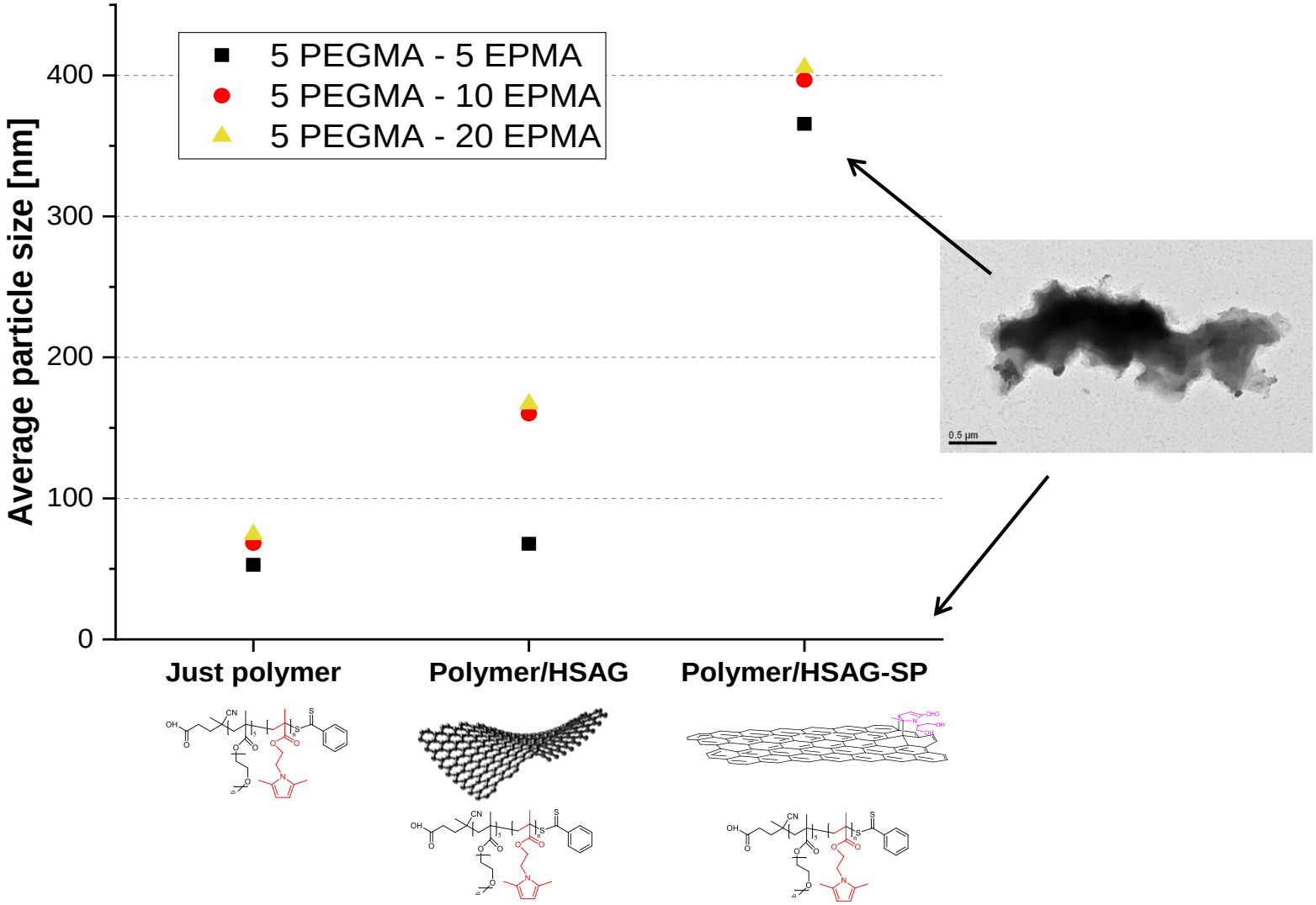
5PEGMA950-p(EPMA)



5PEGMA950

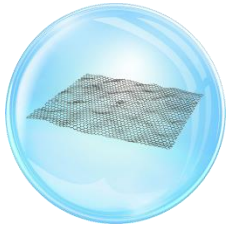
p(EPMA)

Formation of micelles



The adduct between 5PEGMA950-p(EPMA) and graphene layers as nanoreactor for organic synthesis

The *Dropcat catalyst*



Synthesis of imines with the *Dropcat catalyst*

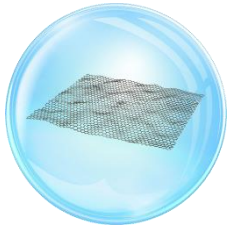
Why imines?

- They are involved in the synthesis of drugs.

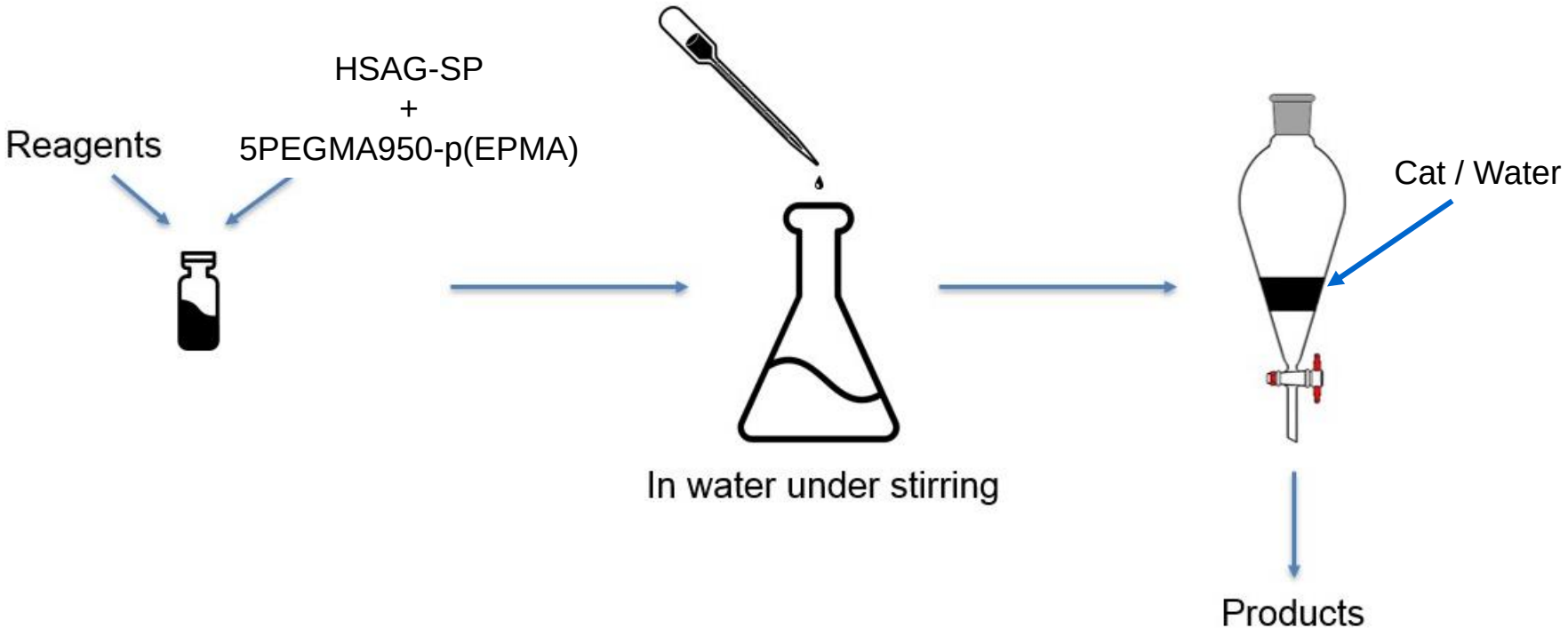
  e.g.: benzodiazepines, antimalarial

- They can be used in vulcanization systems of tyre compounds

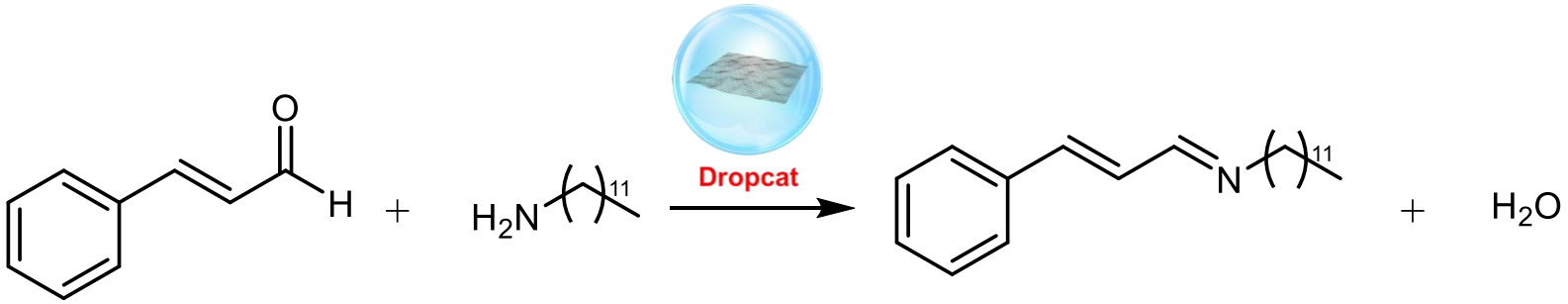
Large scale applications



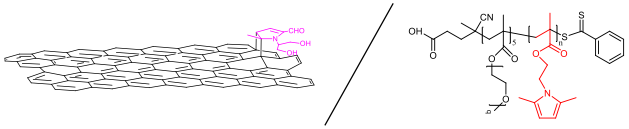
Synthesis of imines with the *Dropcat catalyst*



Synthesis of imines with the *Dropcat catalyst*

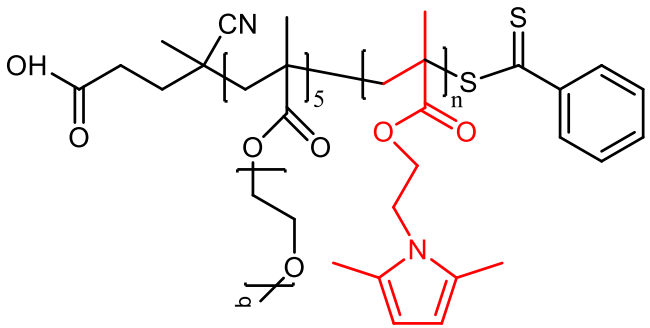


time (min)	Selected system	T (°C)	Yield (%)
240	-	180	60
5	5PEGMA-5EPMA/HSAG-SP	25	98



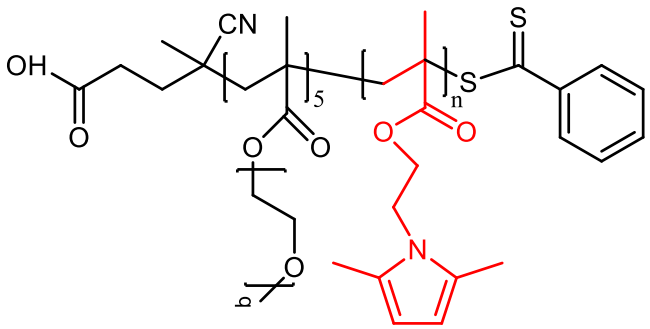
U. Capasso Palmiero, M. Sponchioni, F. Margani, D. Moscatelli, M. Galimberti, V. Barbera *Small, 16(40), 2001207 (2020)*

What is the role of the monomer?

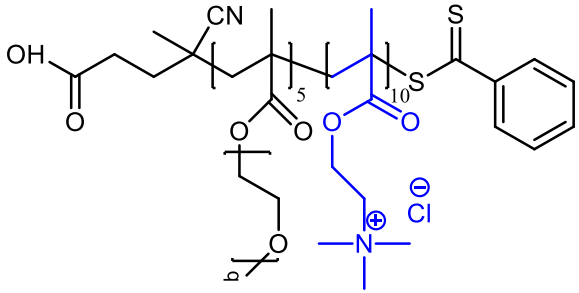


5PEGMA-5EPMA

What is the role of the monomer?

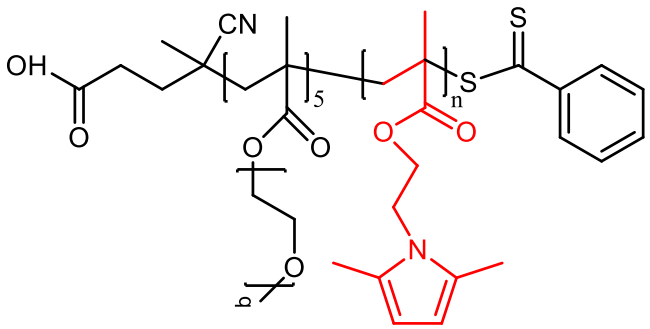


5PEGMA-5EPMA

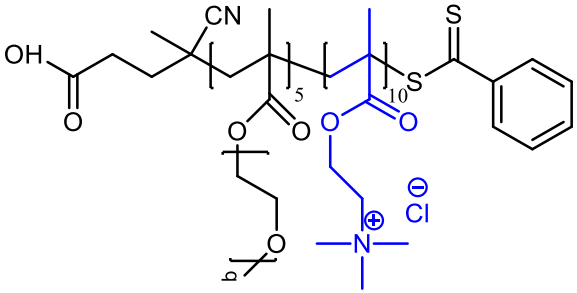


5PEGMA-10TMAEMA

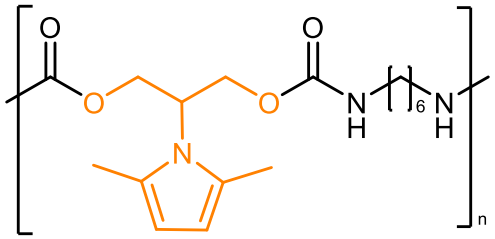
What is the role of the monomer?



5PEGMA-5EPMA



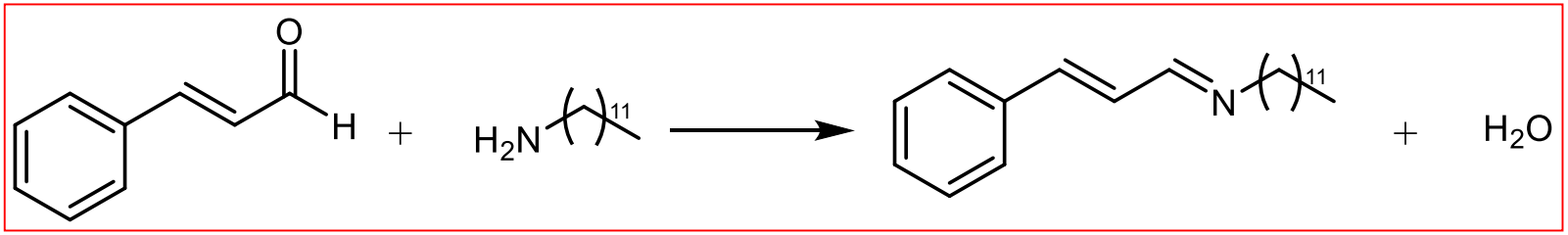
5PEGMA-10TMAEMA

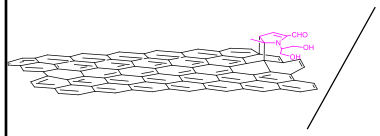
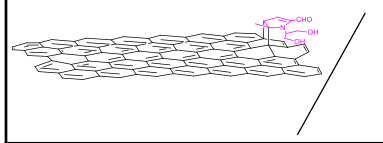
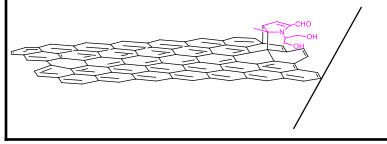


PU-SP

Mn = 1430 Da

The role of the monomer. Dropcat catalysts with different polymers



Selected system	Yield (%)
 5PEGMA-5EPMA/HSAG-SP	**98**
 5PEGMA-TMAEMA/HSAG-SP	23
 PU-SP/HSAG-SP	52

Temperature = 25°C

time = 5 minutes

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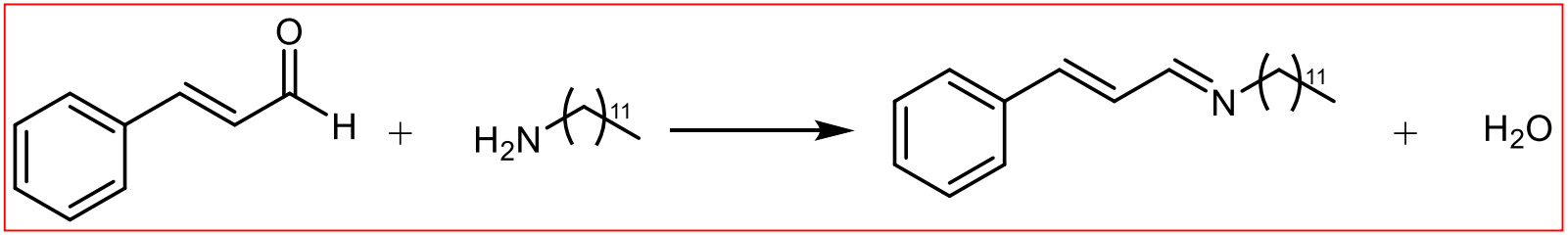
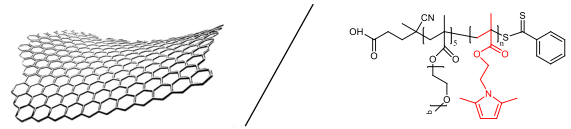
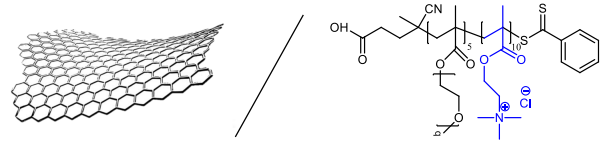
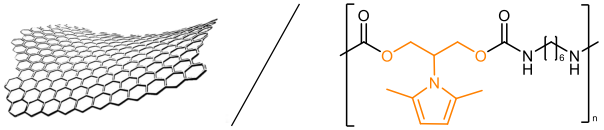
The role of graphene layers. Dropcat catalysts with pristine nanographite



Selected system	Yield (%)
 5PEGMA-5EPMA/HSAG	-
 5PEGMA-TMAEMA/HSAG	30
 PU-SP/HSAG	50

Temperature = 25°C

time = 5 minutes

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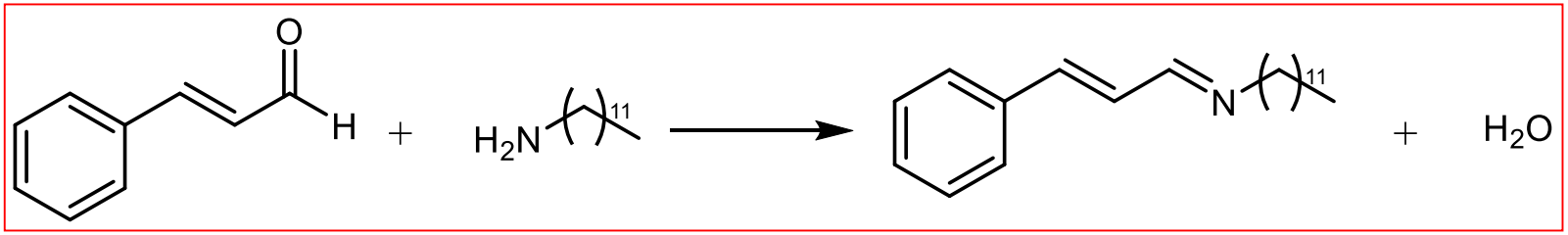
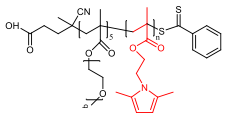
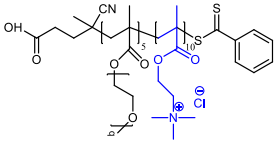
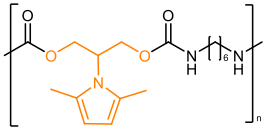
The role of graphene layers. Dropcat catalysts without graphene layers



Selected system	Yield (%)
 5PEGMA-5EPMA	10
 5PEGMA-TMAEMA	23
 PU-SP	53

Temperature = 25°C

time = 5 minutes

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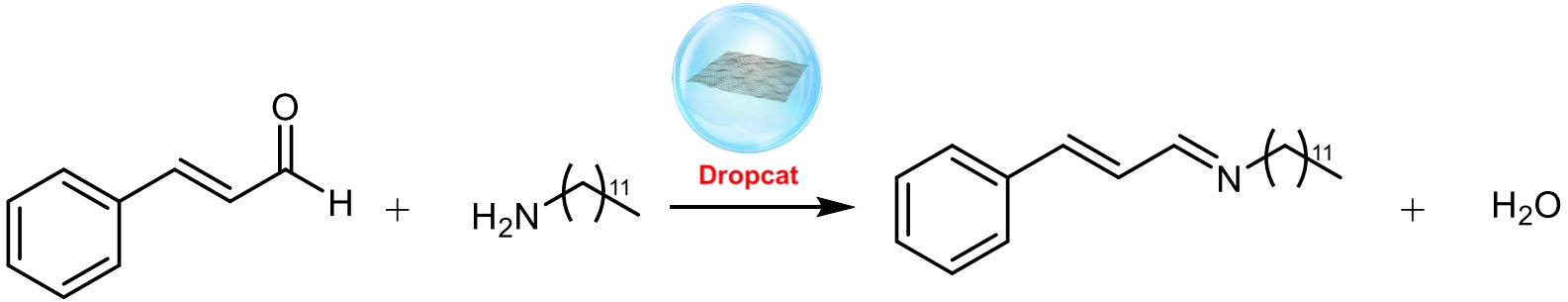
The synergy of covalent and supramolecular functionalization



time (min)	Selected system	T (°C)	Yield (%)
240	-	180	60
5	5PEGMA-5EPMA	25	10
5	5PEGMA-5EPMA/HSAG	25	-
5	**5PEGMA-5EPMA/HSAG-SP**	**25**	**98**

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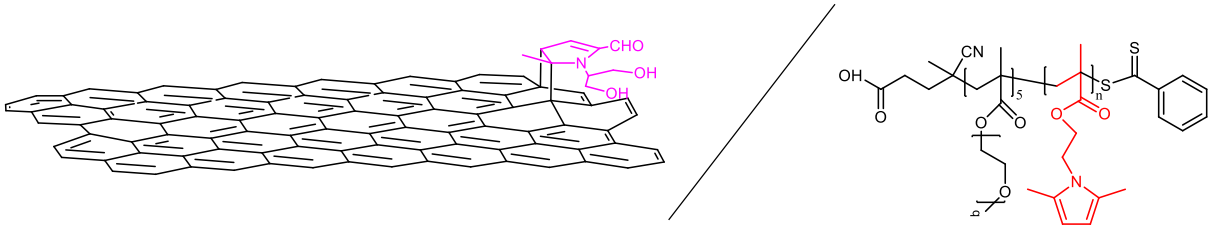
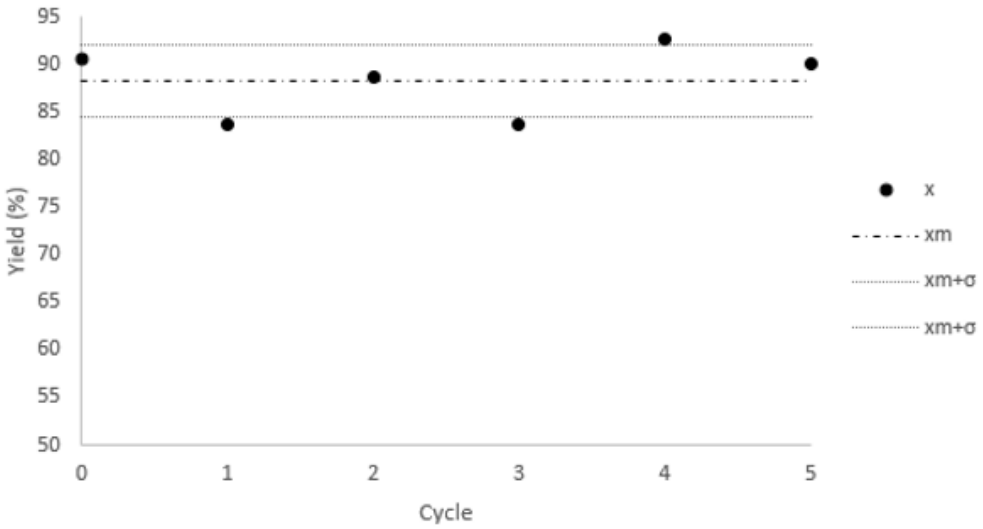
Recyclability and catalytic activity

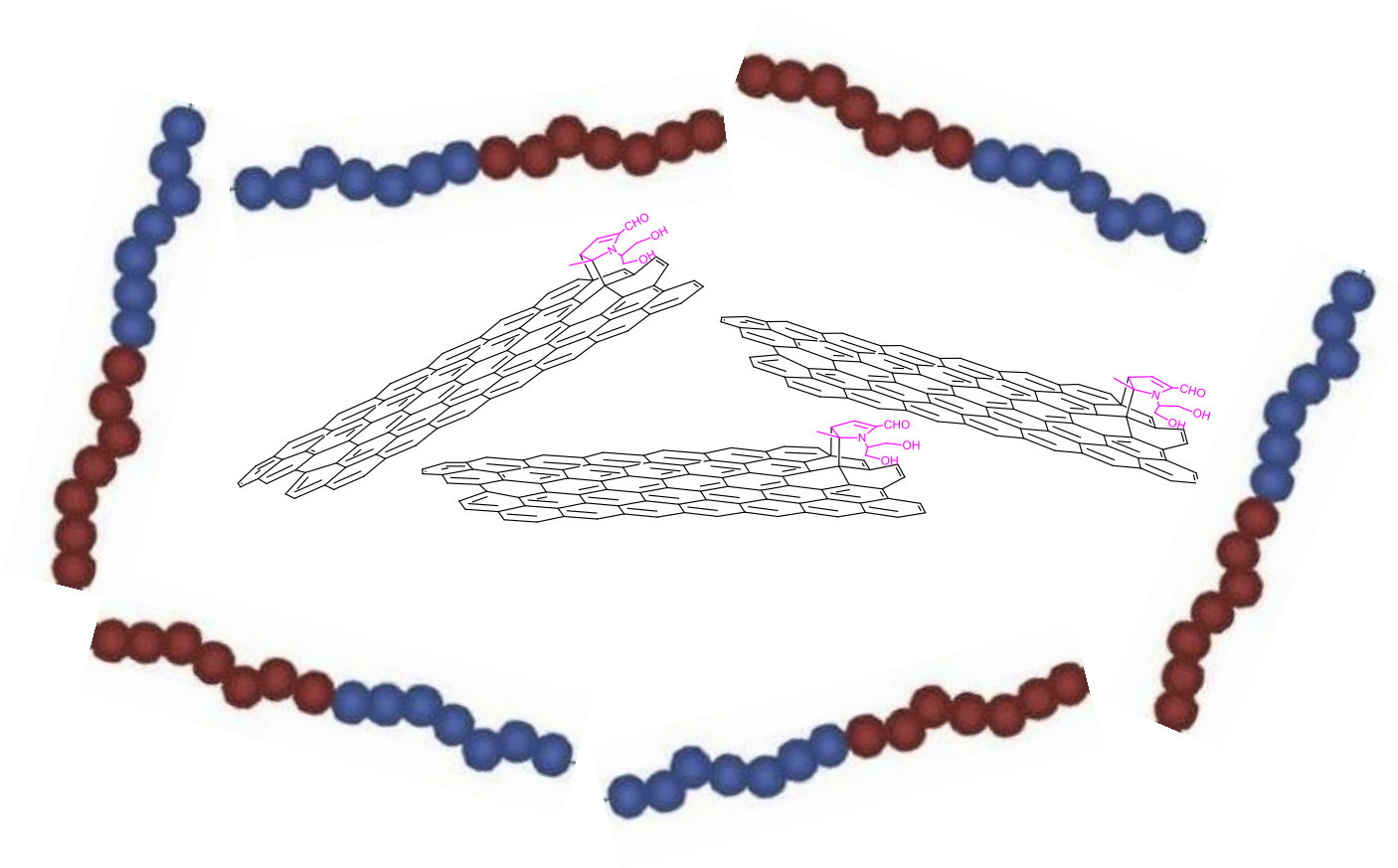


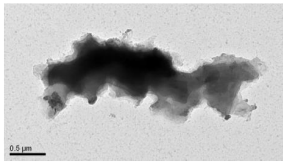
5PEGMA-5EPMA/HSAG-SP

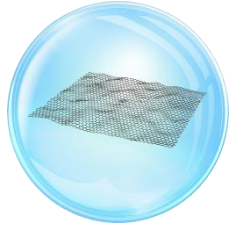


EPMA based polymer reusability

Drop Cat as self assembled nanoreactor

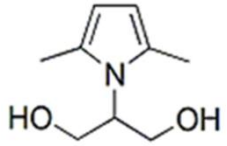




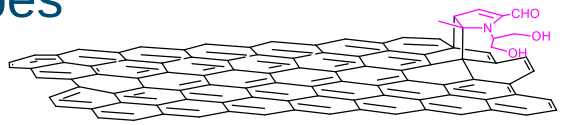


Conclusions

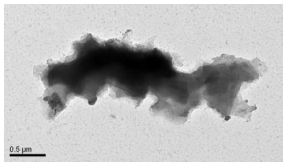
- Biosourced *Janus* molecule



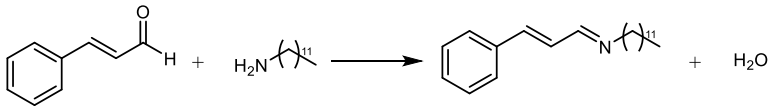
- The functionalization of sp^2 carbon allotropes



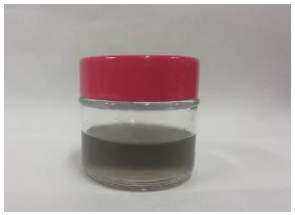
- Waterborne nanoreactors



- The nanoreactors for organic synthesis in water



98% yield @25°C, 5 min



Gel

Aerogel

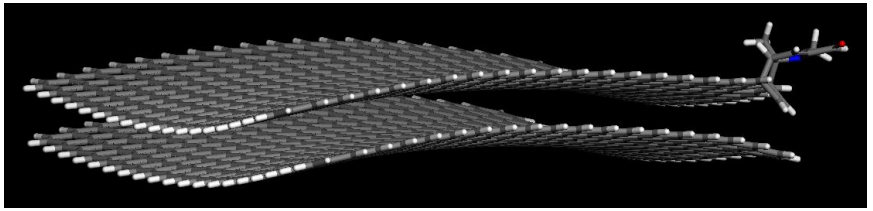
Powder

Perspectives

Theoretical study based on Molecular Mechanics and Molecular Dynamics simulations of:

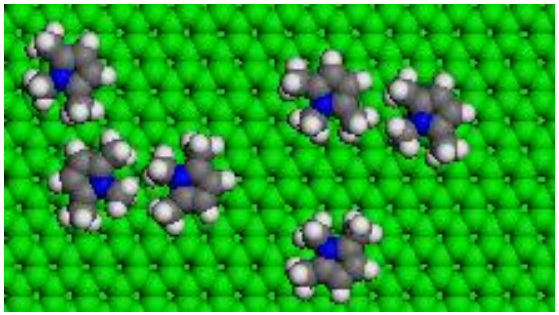
- Few layers of *nano*graphene

☞ importance of covalent functionalization



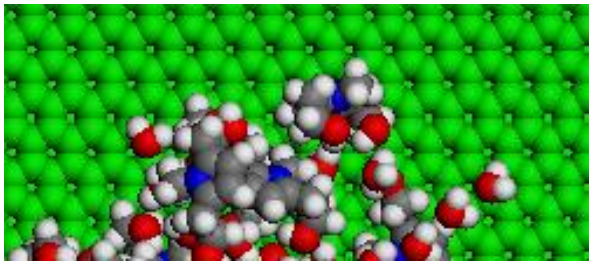
- Adsorption of pyrrole compound

☞ role of π-π interactions



- Formation of micelles

☞ Role of water solvent



Raffaini, G.; Ganazzoli, F. ***Macromol. Biosci.* 2007, *7*, 552.**
Understanding the performance of biomaterials through molecular modeling: Crossing the bridge between their intrinsic properties and the surface adsorption of proteins

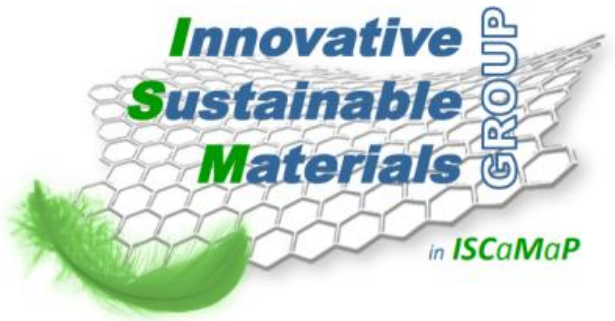
Acknowledgments

Gianfranco Savino, Enrico Valentini (Politecnico di Milano)

Maria Farina and Giulio Natta

Thanks

for your attention!



instagram: @ismaterials.polimi