University of Salerno

Department of Chemistry and Biology

New Technologies in Tires: From Layered Nanofillers to Metathesis Reactions

Ph.D. in Chemistry

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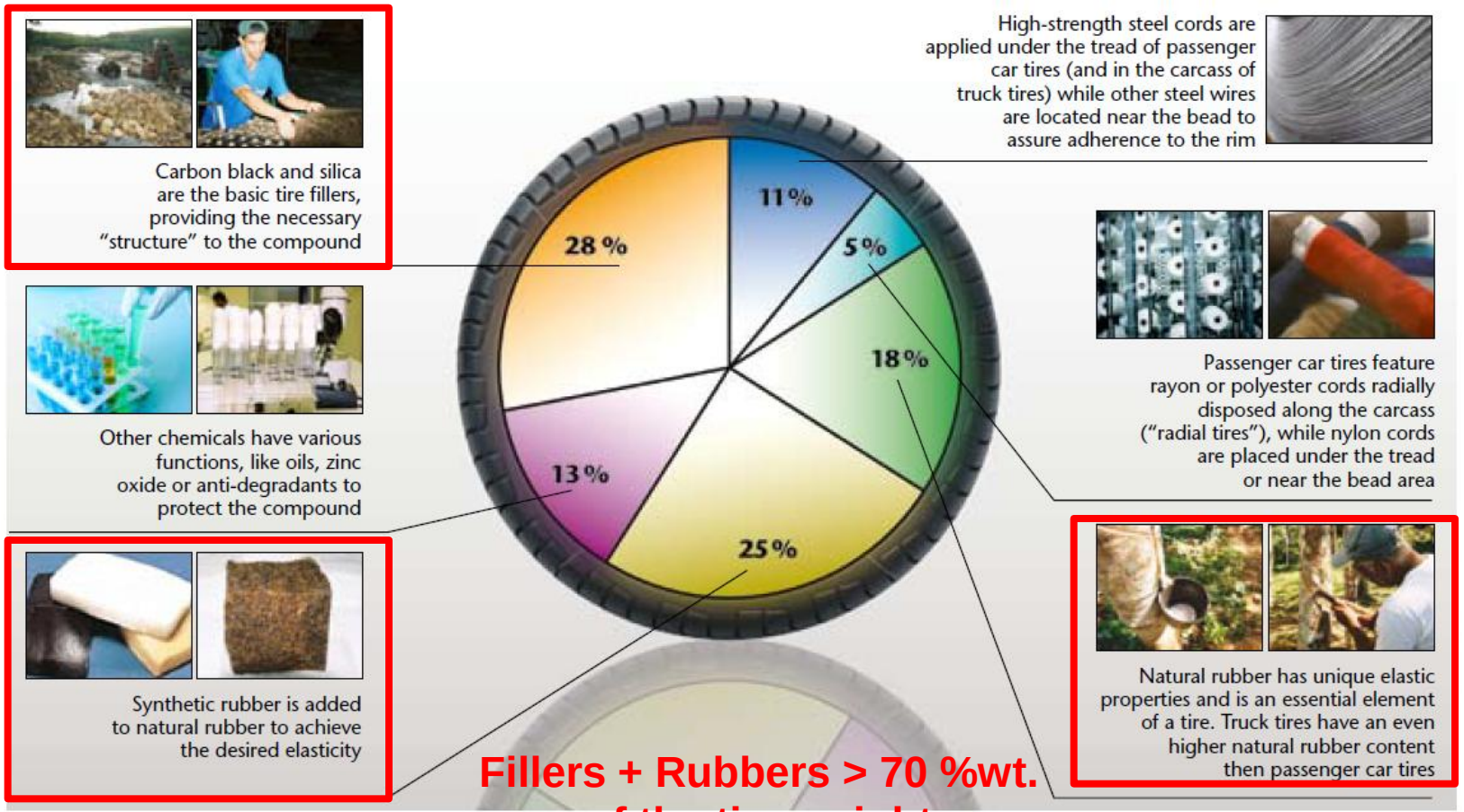
XII Cycle 2011-2014

Fisciano, February 25, 2014

Contents

Tires are Composite Artifacts

A vehicle tire generally contains synthetic rubber, natural rubber, carbon black, steel cord, polyester, nylon, steel bead wire, silica and different kinds of chemicals, waxes, oils and pigments.

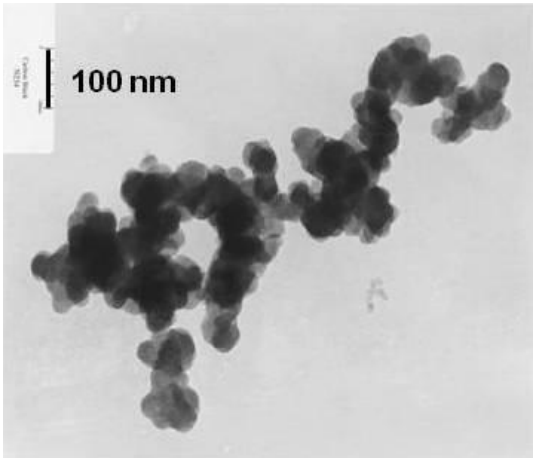


Fillers + Rubbers > 70 %wt. of the tire weight

Managing End-of-Life Tires Full Report, *World Business Council for Sustainable Development – Tire Industry Project,* **2008**, pp. 2

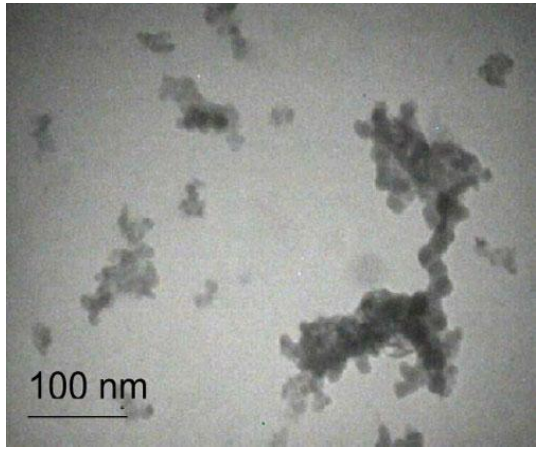
Nanotechnologies and Nanofillers

Carbon Black



Standard Nanofillers for Rubbers

Silica



A. I. Medalia, G. Kraus, in *The Science and Technology of Rubber Second Ed. Elsevier Academic Press* **1994,** Chapter 8, p. 387.

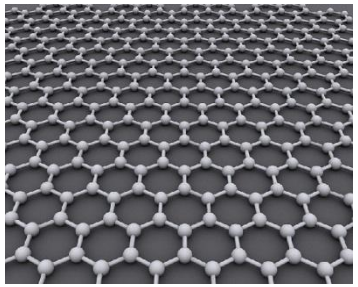
Tire technology has always been based on Nanotechnology!

New Nanofillers

- Extended rubber-filler interfaces
- Enhanced Mechanical Properties
- Lower Filler Percolation Threshold
- Reduced Tire Weight

Fillers with layers of sp^2-bonded C atoms

Graphene

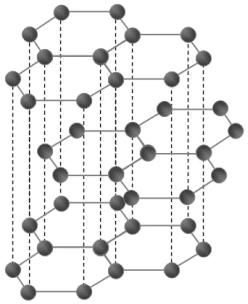


Single layer

2D

piled with
…ABAB… stacking

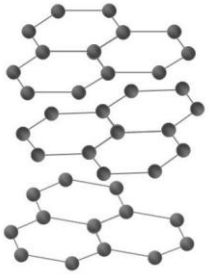
Hexagonal graphite



3D

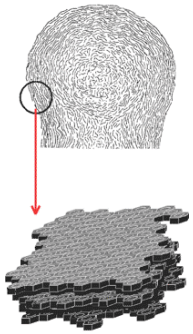
lack of
…ABAB… stacking

Turbostratic structures



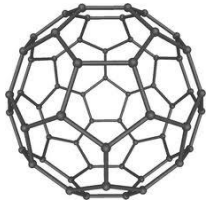
Randomly arranged

Carbon Black



wrapped

Fullerenes

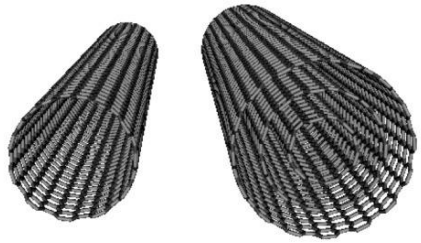


Buckyballs

0D

rolled

Carbon nanotubes

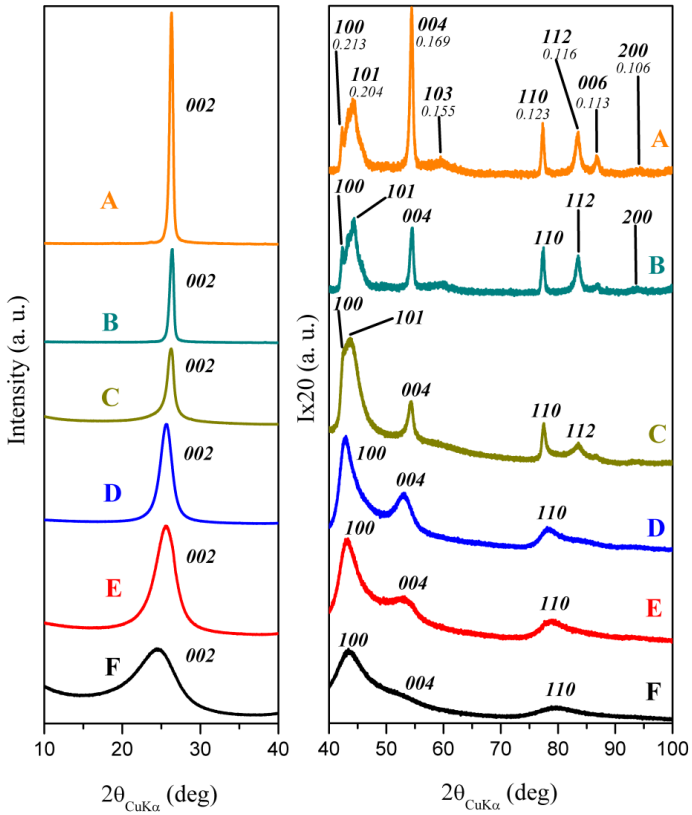


SWCNT **MWCNT**

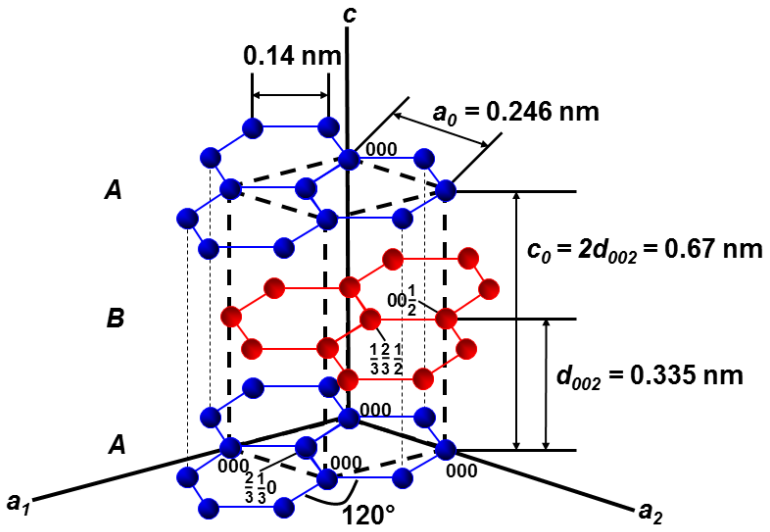
1D

A. K. Geim and K. S. Novoselov, *Nature Materials*, *6*, 183-191, **2007**

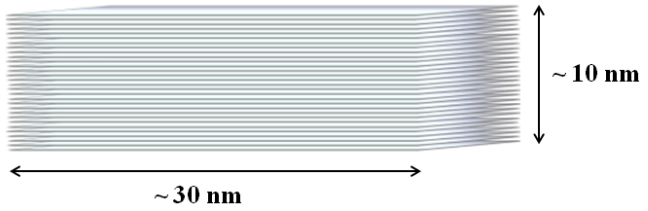
Graphites Characterization



- **A**, **B** thermally treated graphites
- **C** milled graphite
- **D**, **E** cokes
- **F** carbon black



sample	d_{002} (nm)	$D_\perp$ (nm)	$D_\parallel$ (nm)	$D_\parallel/D_\perp$	$\varepsilon_\perp$ (%)	$\varepsilon_\parallel$ (%)	$\varepsilon_\perp/\varepsilon_\parallel$
A	0.339	20.3	44.5	2.2	0.047	0.059	0.8
B	0.339	16.8	36.4	2.2	0.060	0.059	1.0
C	0.339	9.8	30.2	3.1	0.107	0.073	1.5
D	0.34_7	5.9	6.5	1.1	0.38	0.33	1.1
E	0.34_8	3.5	3.6	1.0	0.78	0.50	1.5
F	0.36_5	1.9	2.9	1.5	1.6	0.67	2.4



High shape anisotropy graphite (G)

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

Graphite Oxide

= 0.339 nm = d_{002}

G

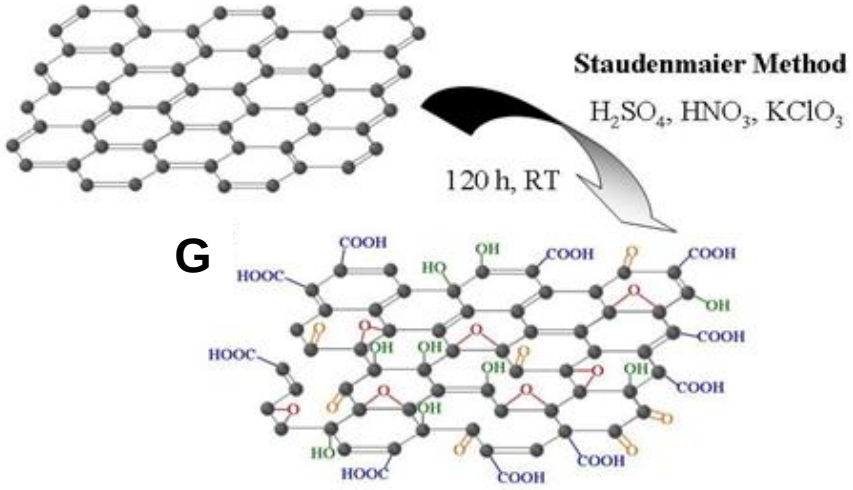
H_2SO_4, HNO_3, $KClO_3$

Staudenmaier L.
Ber Dtsch Chem Ges
1898, *31*:1481

= 0.84 nm = d_{001}

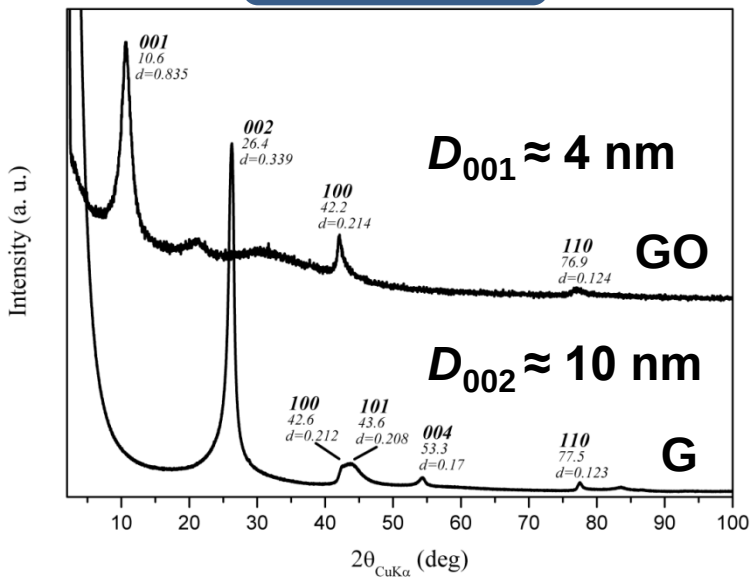
GO

Cationic Exchange Capacity
(C.E.C) = 7.3 mmol/g

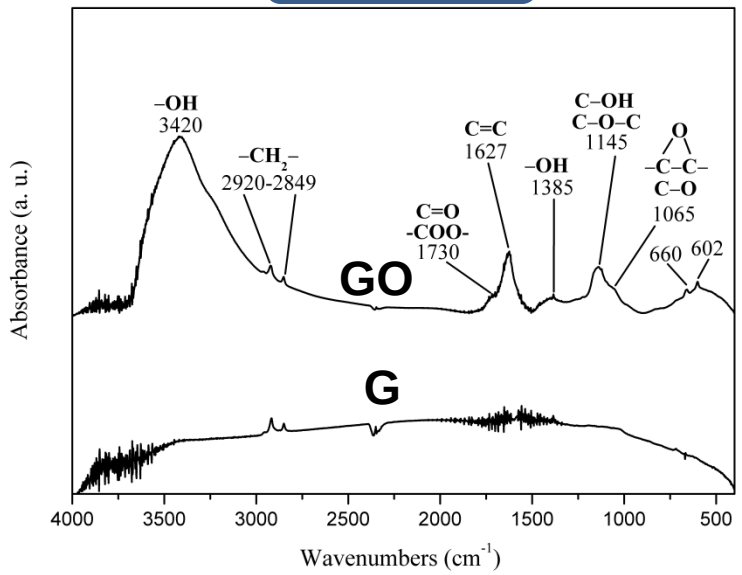


GO: Graphite Oxide (C/O ~ 1.6)

WAXD Analysis



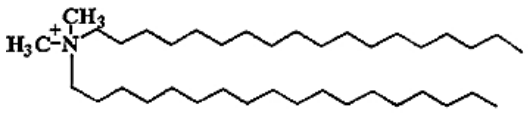
FTIR Analysis



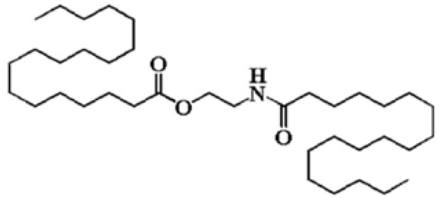
Graphite Oxide Intercalation Compounds

GO: Graphite Oxide

+ NaOH +



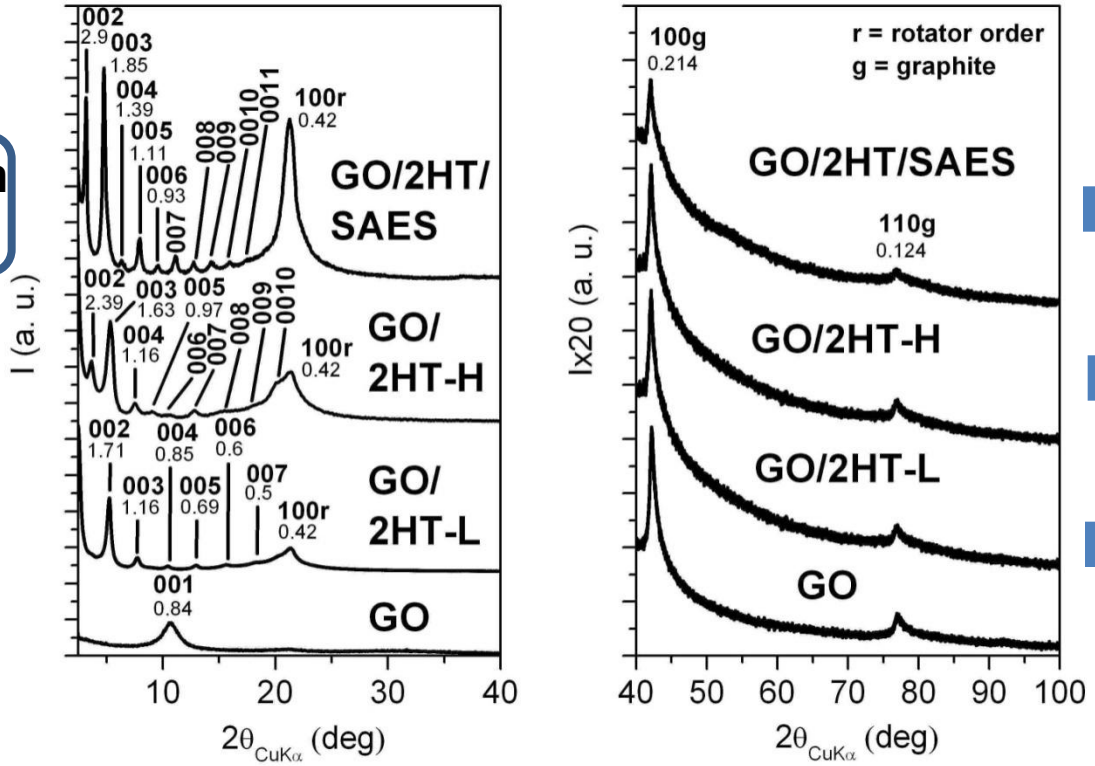
2HT: Di(hydrogenated tallow) dimethyl ammonium



SAES: 2-stearamidoethyl stearate

WAXD Analysis

$D_{100g} \approx 30$ nm
$D_{100r} \approx 10$ nm



$d_{001} \approx 5.8$ nm
$D_{001} \approx 42$ nm

$d_{001} \approx 4.8$ nm
$D_{001} \approx 16$ nm

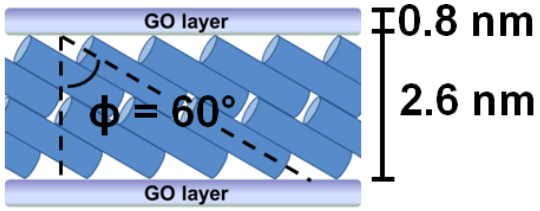
$d_{001} \approx 3.4$ nm
$D_{001} \approx 14$ nm

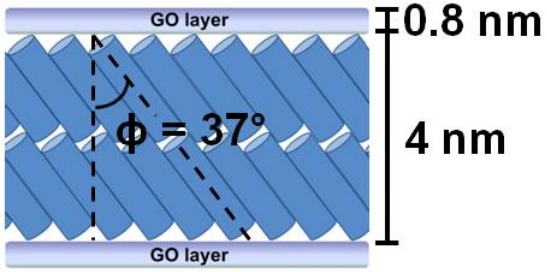
M. Mauro, M. Maggio, V. Cipolletti, M. Galimberti, P. Longo, G. Guerra *Carbon,* ***2013****, 61, 395-403*

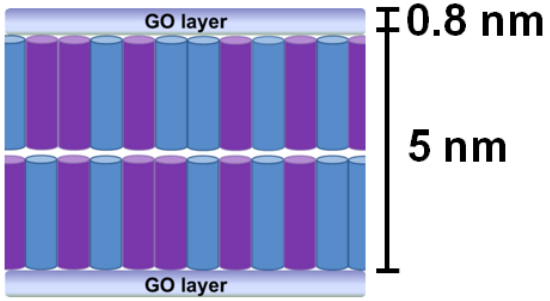
GOICs: Structures

d_{001} = 3.4 nm	d_{001} = 4.8 nm	d_{001} = 5.8 nm

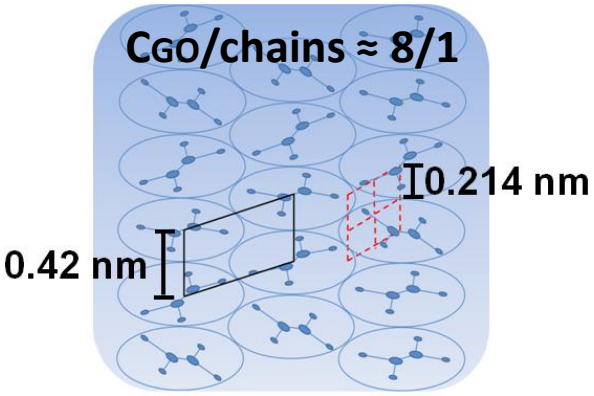
Lateral view

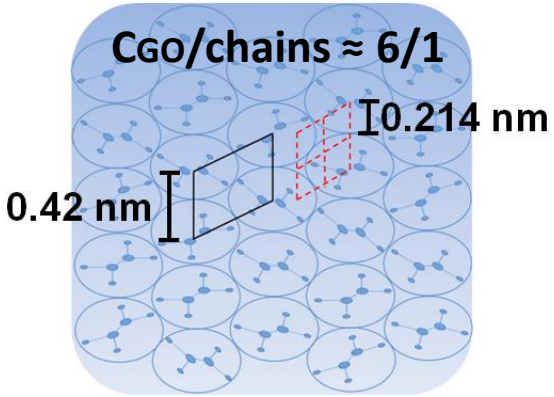


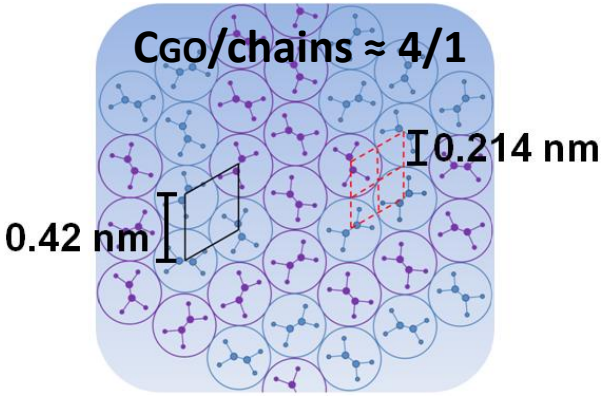




Top view







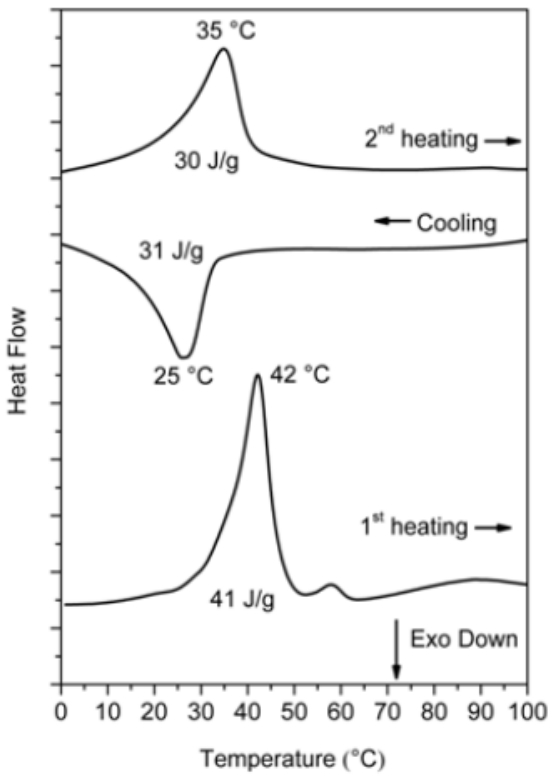
GO/2HT-L | **GO/2HT-H** | **GO/2HT/SAES**

Tilted Bi-layer | **Perpendicular Bi-layer**

= 2HT C18 alkyl chain

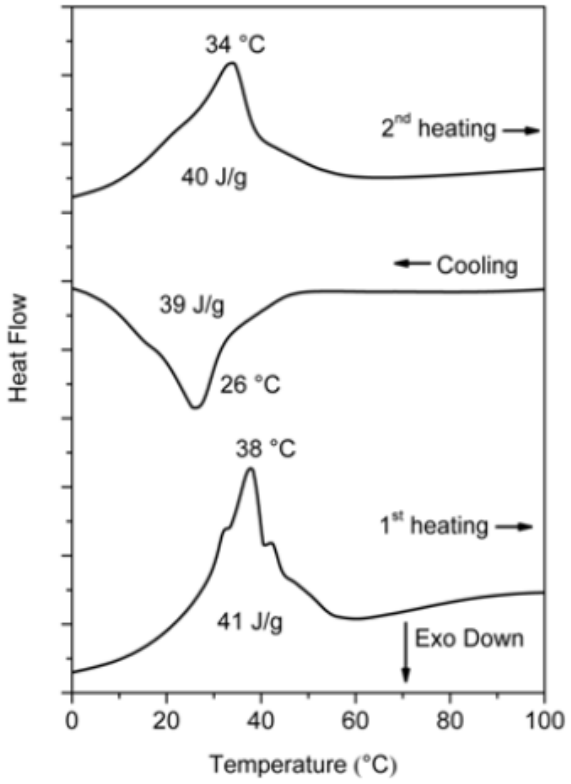
= SAES C18 alkyl chain

GOICs: DSC Analysis



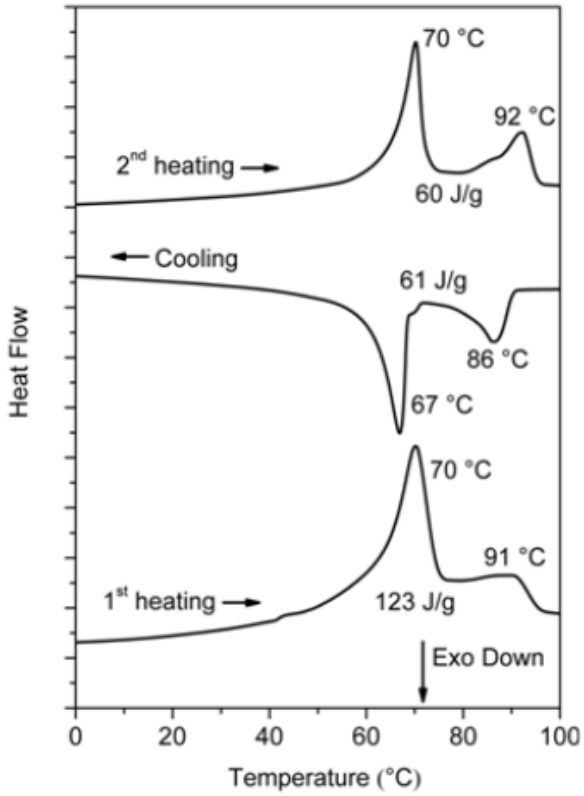
GO/2HT-L

CGO/chains ≈ 8/1



GO/2HT-H

CGO/chains ≈ 6/1



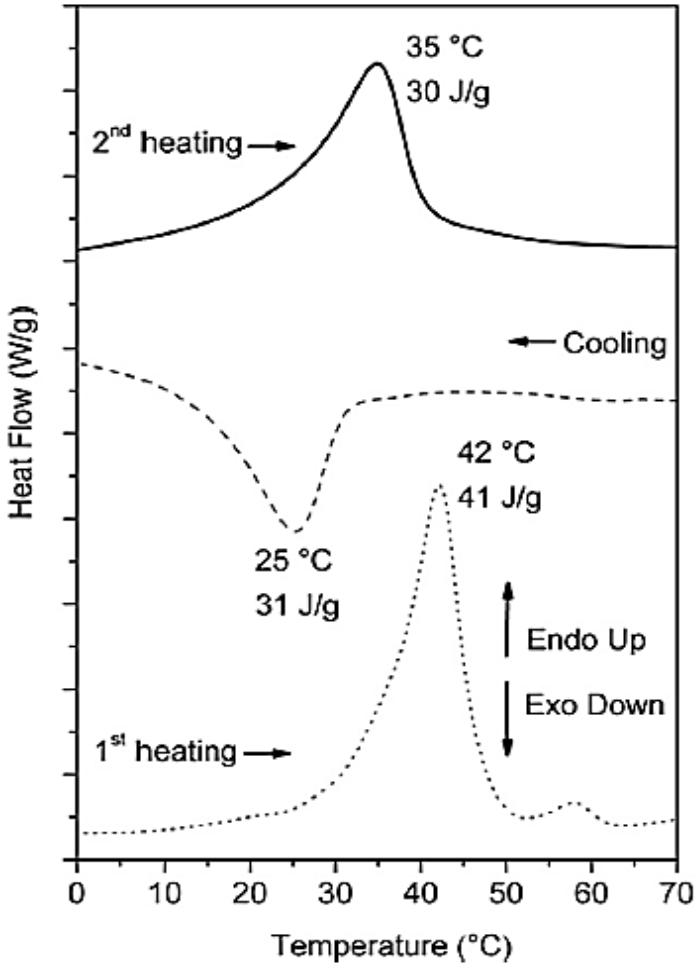
GO/2HT/SAES

CGO/chains ≈ 4/1

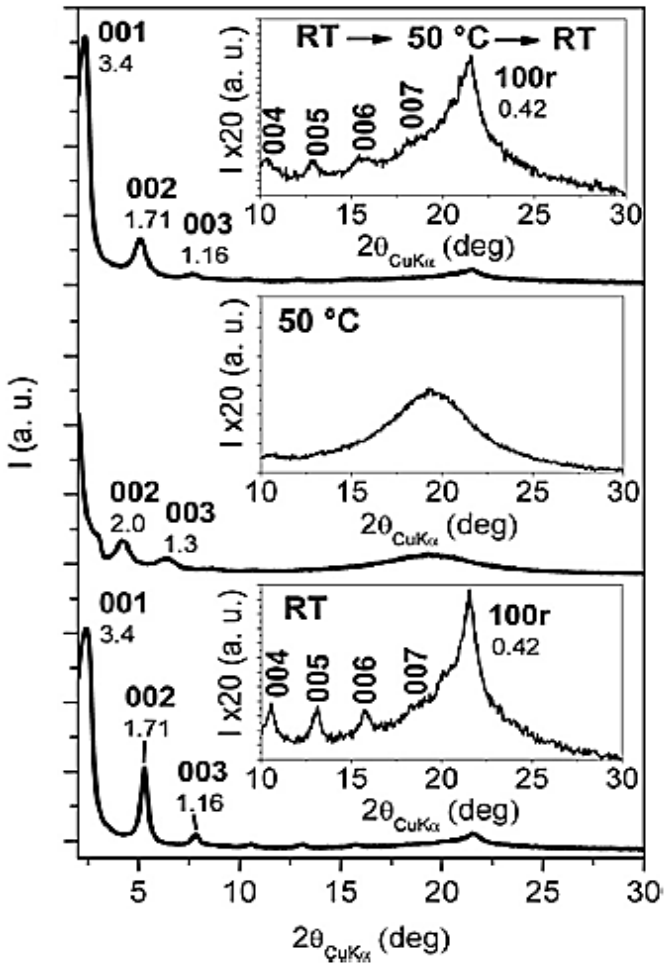
Transition temperatures and melting enthalpies increase with the chains content in the intarlayer space.

GOICs: Structure Reversibility

DSC Analysis



WAXD Analysis

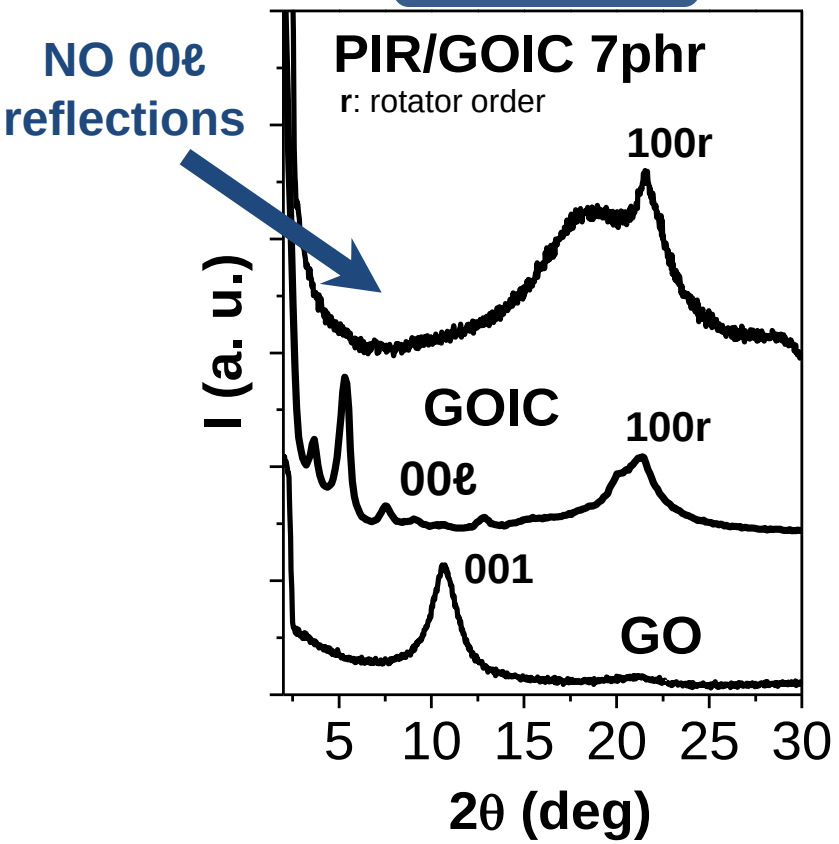


Thermal treatments of GO/2HT-L intercalate

Rubber/GOIC Nanocomposites

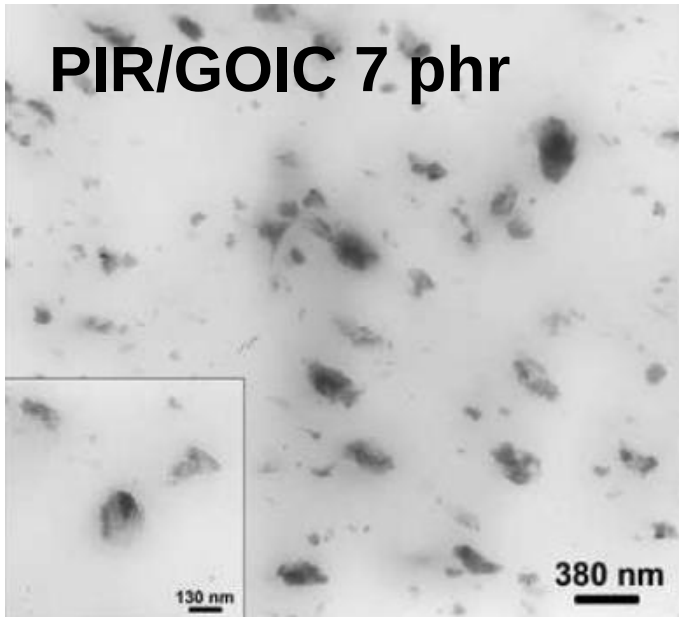
PIR + GOIC powder → **Ball milling** → PIR/GOIC Masterbatch → **Sulfur Additives 170ºC** → Vulcanized PIR/GOIC

WAXD Analysis



phr: parts per hundred grams of rubber

TEM Analysis

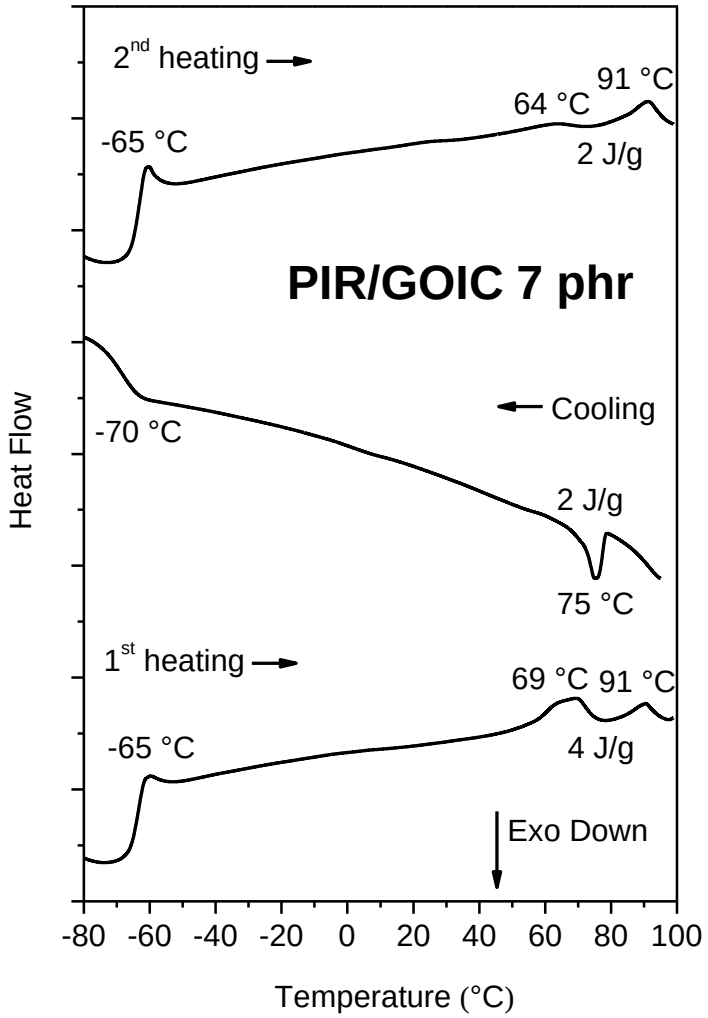


Evenly distributed and prevaingly exfoliated stacks with nanometric dimensions

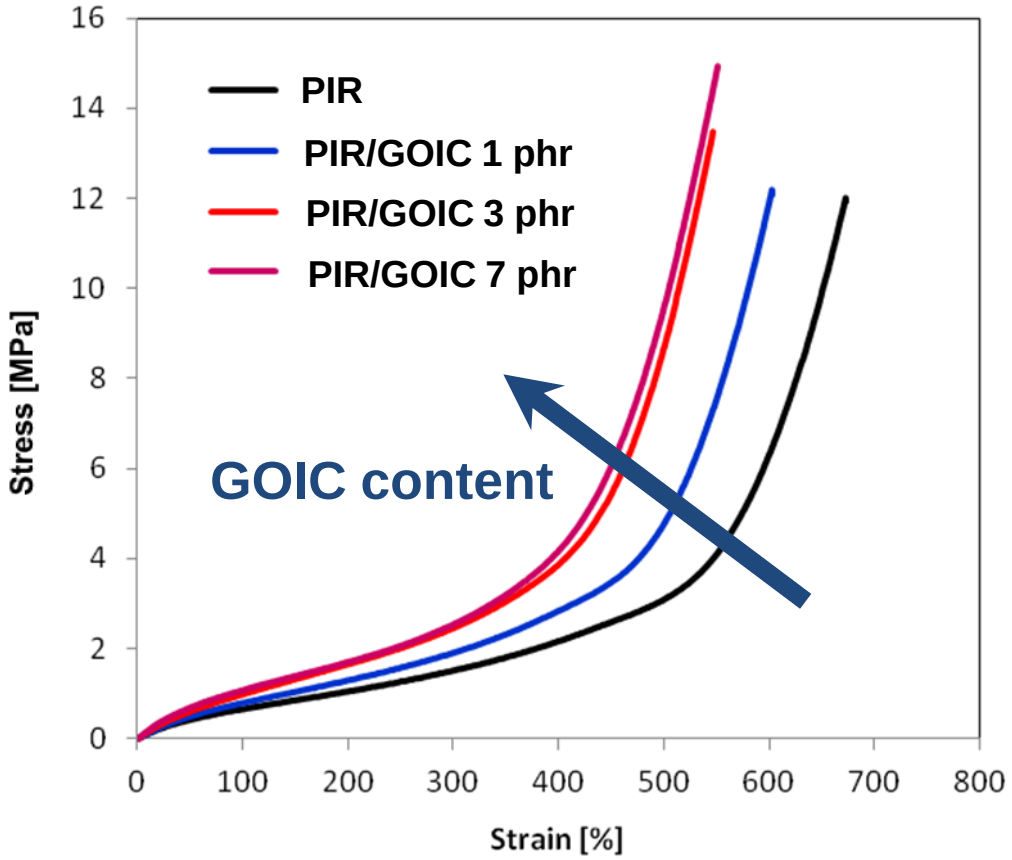
M. Galimberti, V. Cipolletti, M. Mauro, L. Conzatti. *Macromol. Chem. Phys.* **2013**, *214*, 1931–1939

Rubber Nanocomposites Properties

DSC Analysis

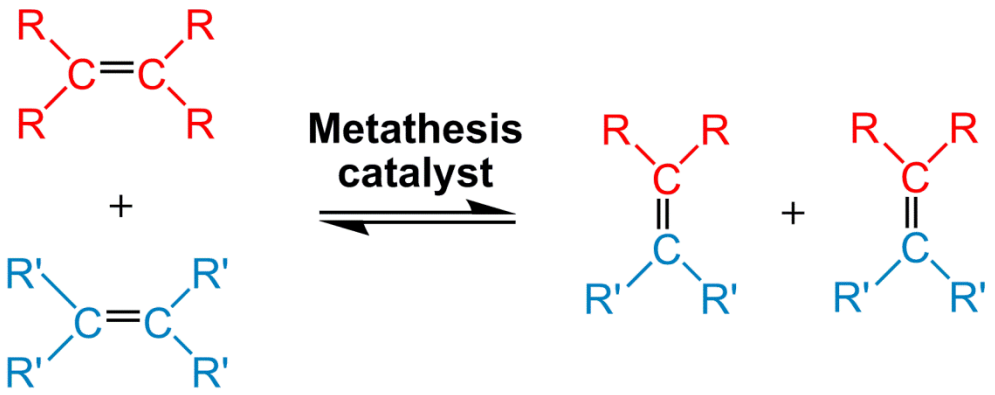


Stress-Strain Analysis



M. Galimberti, V. Cipolletti, M. Mauro, L. Conzatti. *Macromol. Chem. Phys.* **2013**, *214*, 1931–1939

Olefin Metathesis

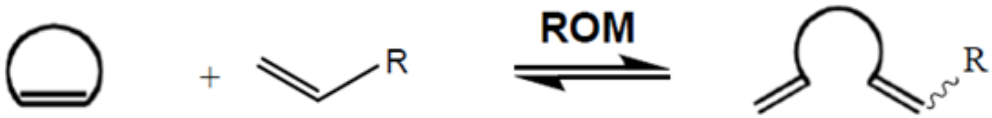


meta = exchange

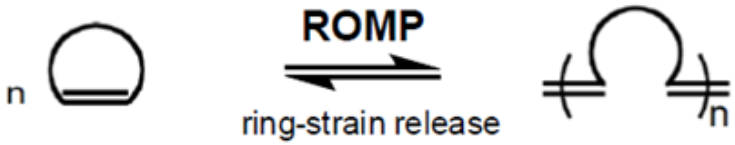
thesis = position

Cross metathesis

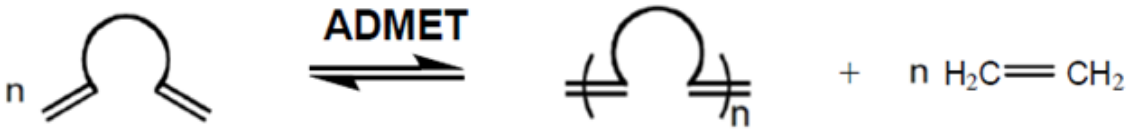
Ring-closing metathesis



Ring-opening metathesis



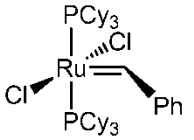
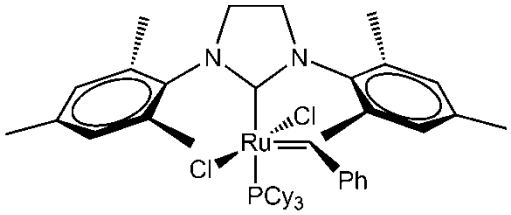
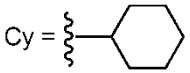
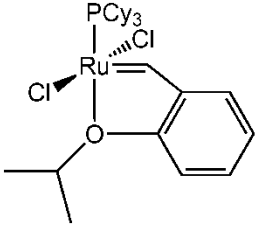
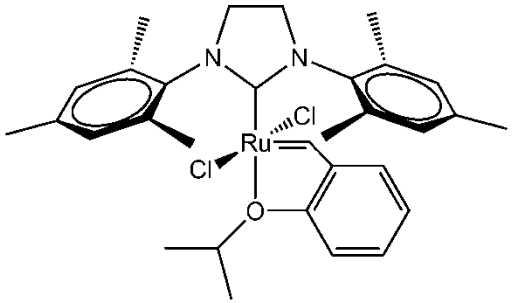
Ring-opening metathesis polymerization



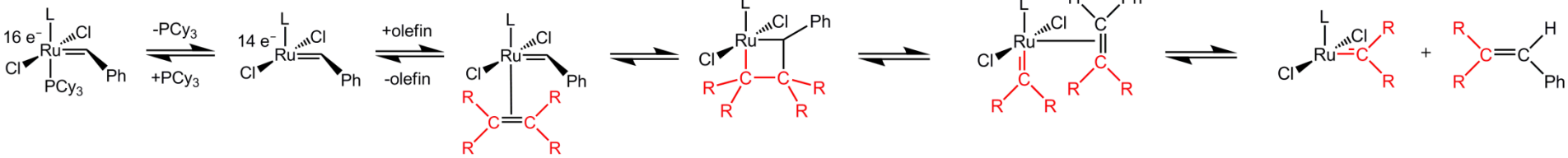
Acyclic diene metathesis polymerization

R. H. Grubbs. *Handbook of Metathesis*; Wiley-VCH:Weinheim, Germany, **2003**

Ruthenium Catalysts

	First Generation	Second Generation
Grubbs Catalysts		
	G1	**G2**
	Cy = 	
Hoveyda-Grubbs Catalysts		
	HG1	**HG2**

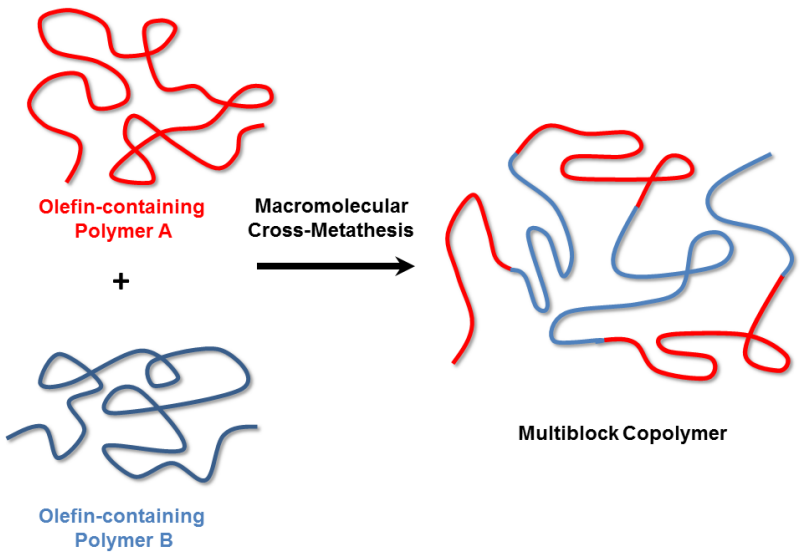
Mechanism



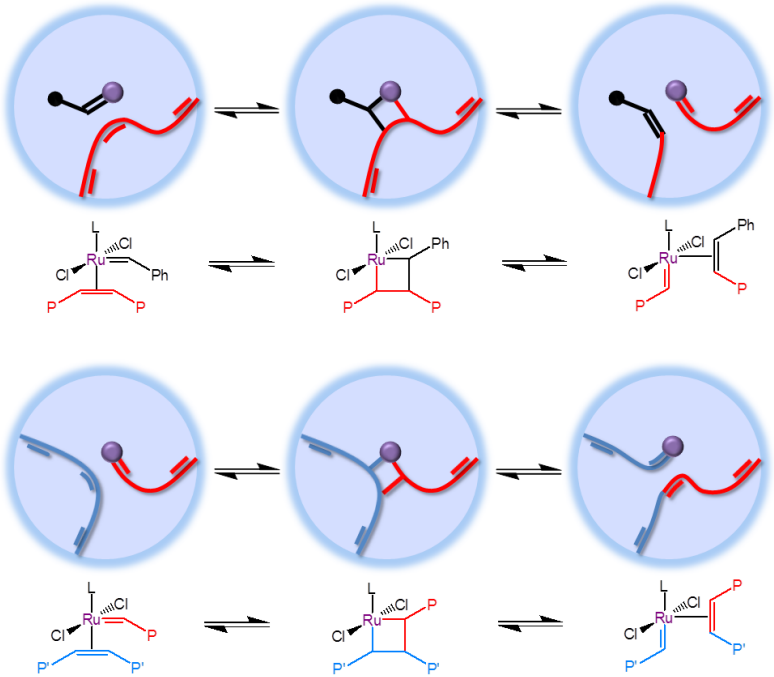
P. Schwab, M. B. France, J. W. Ziller, R. H. Grubbs. *Angew. Chem. Int. Ed.* **1995**, *34*, 2039-2041

P. Jean-Louis Hérisson, Y. Chauvin. *Die Makromolekulare Chemie* **1971**, *141*, 161-176

Macromolecular Cross-Metathesis

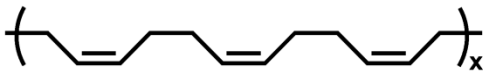


H. Otsuka, T. Muta, M. Sakada, T. Maeda, A. Takahara. *Chem. Commun.* **2009**, 1073–1075



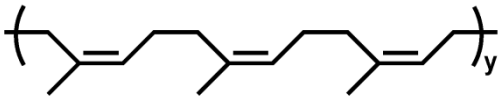
Y. X. Lu, F. Tournilhac, L. Leibler, Z. Guan. *J. Am. Chem. Soc.* **2012**, *134*, 8424-8427

Objective



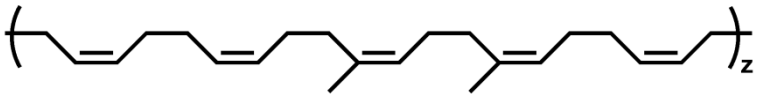
Polybutadiene (PBR)

+



Polyisoprene (PIR)

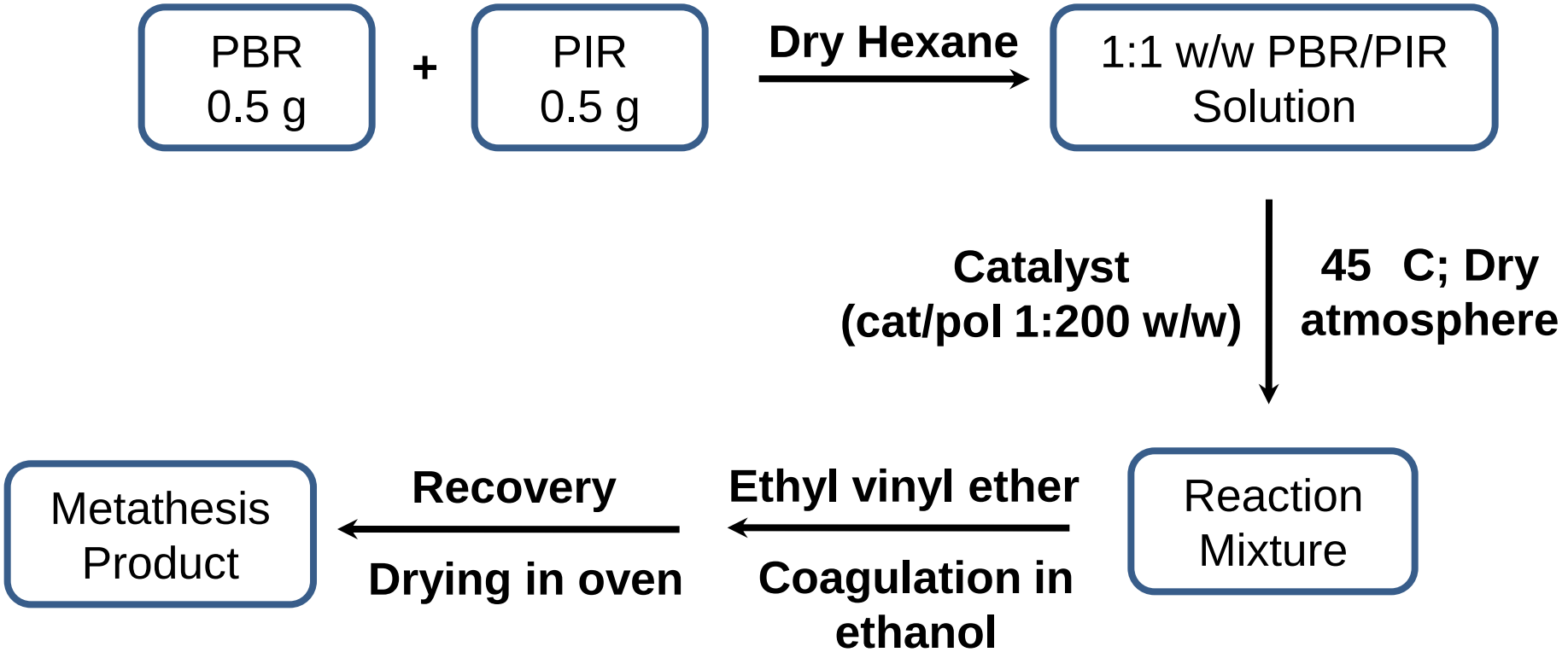
Catalyst



High *cis* PBR-PIR Copolymers

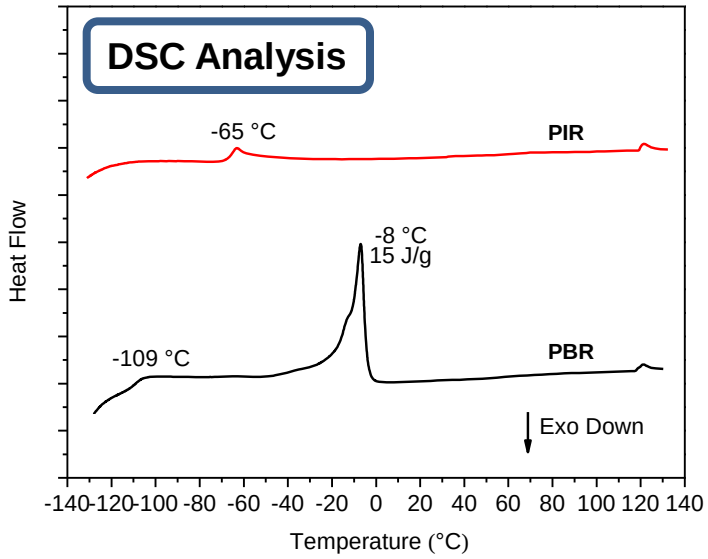
Compatibilizers for PBR/PIR Mixtures

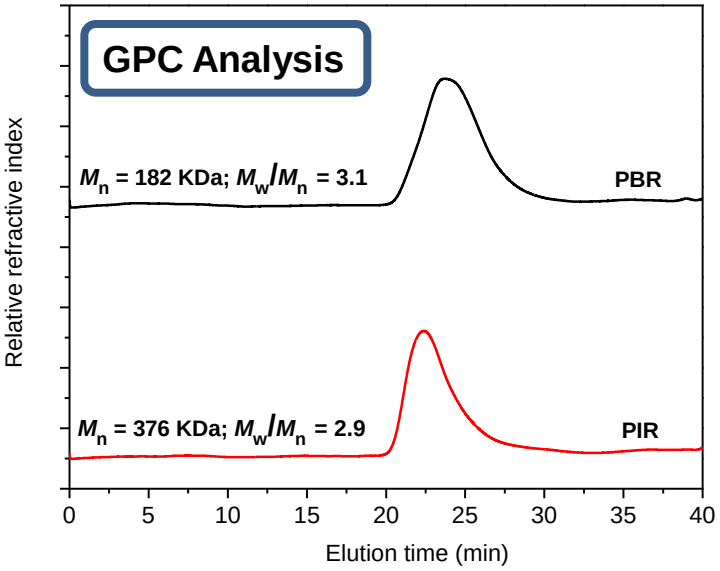
Cross-Metathesis Experimental Procedure

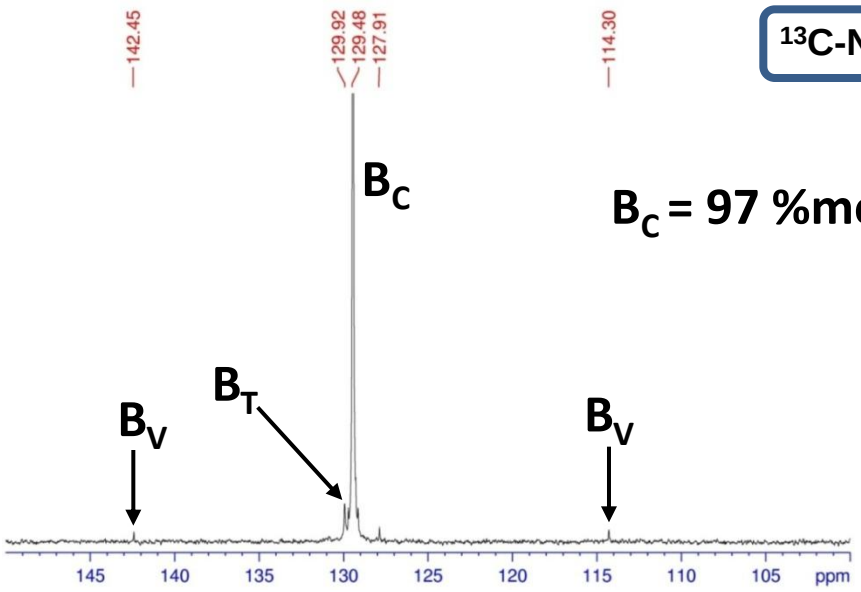


Preliminar Optimization: **10g product, cat/pol 1:1000 w/w, in air**

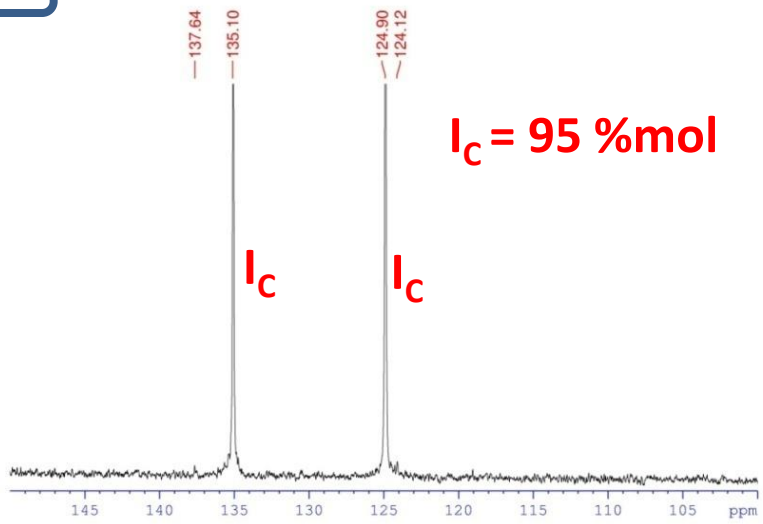
Starting Homopolymers







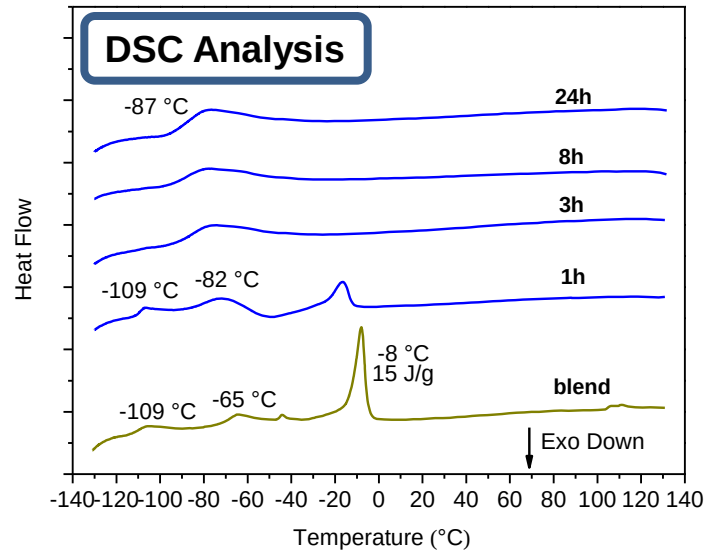
B_C = 97 %mol

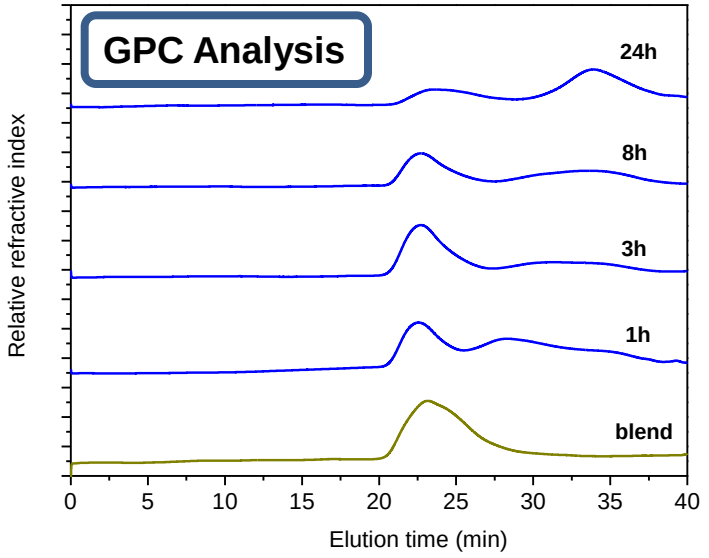


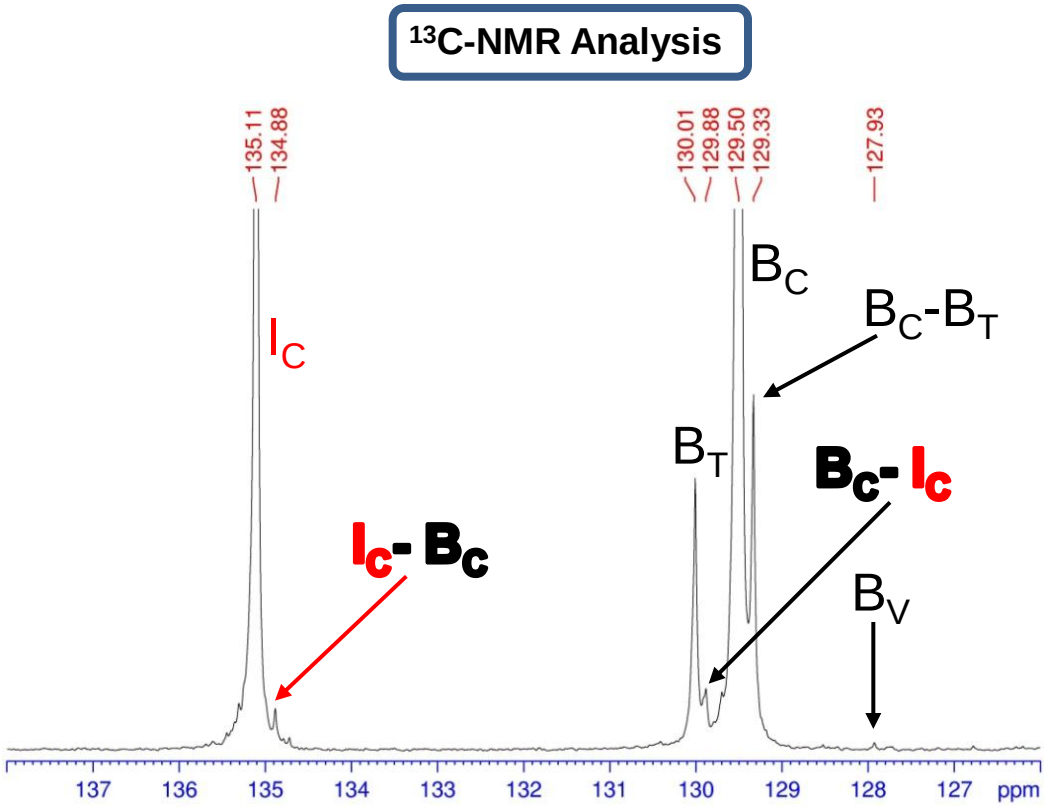
I_C = 95 %mol

K. Matsuzaki, T. Uryu, T. Asakura. NMR Spectroscopy and Stereoregularity of Polymers. *Japan Scientific Societies Press*, pp. 41–50, **1996**

Products from 1st Generation Catalysts







Molar Ratios

Feed

PIR/PBR = 45/55

B_C/B_T = 97/3

I_C/I_T = 95/5

Product at 8h

PIR/PBR = 60/40

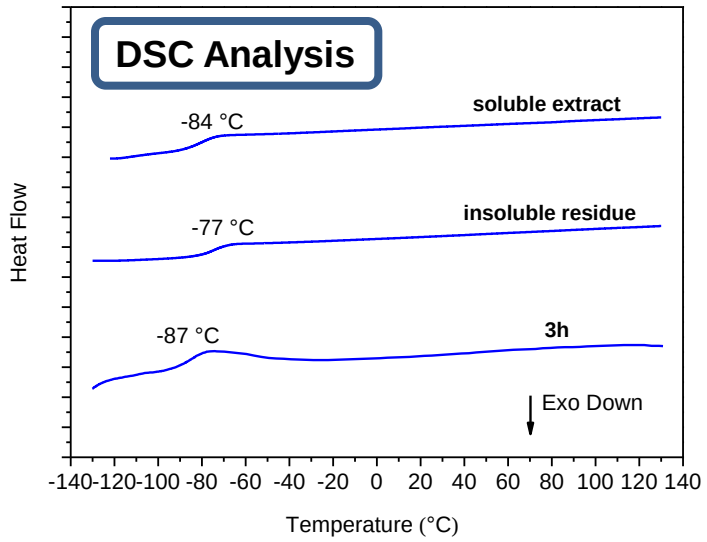
B_C/B_T = 90/10

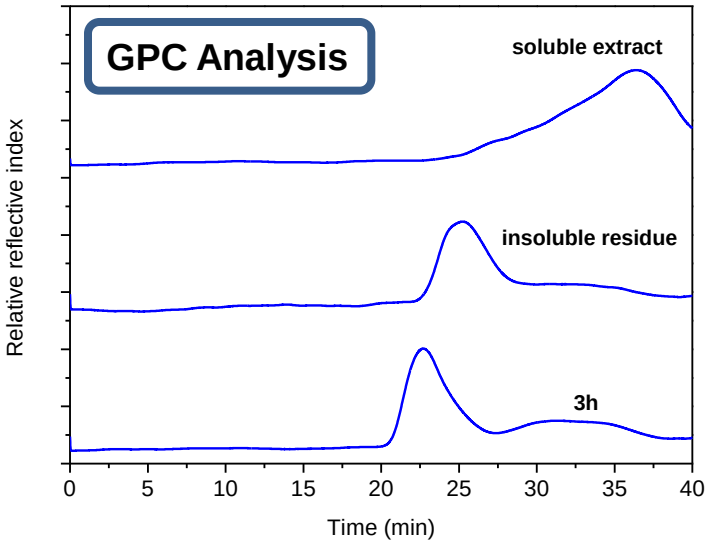
I_C/I_T = 98/2

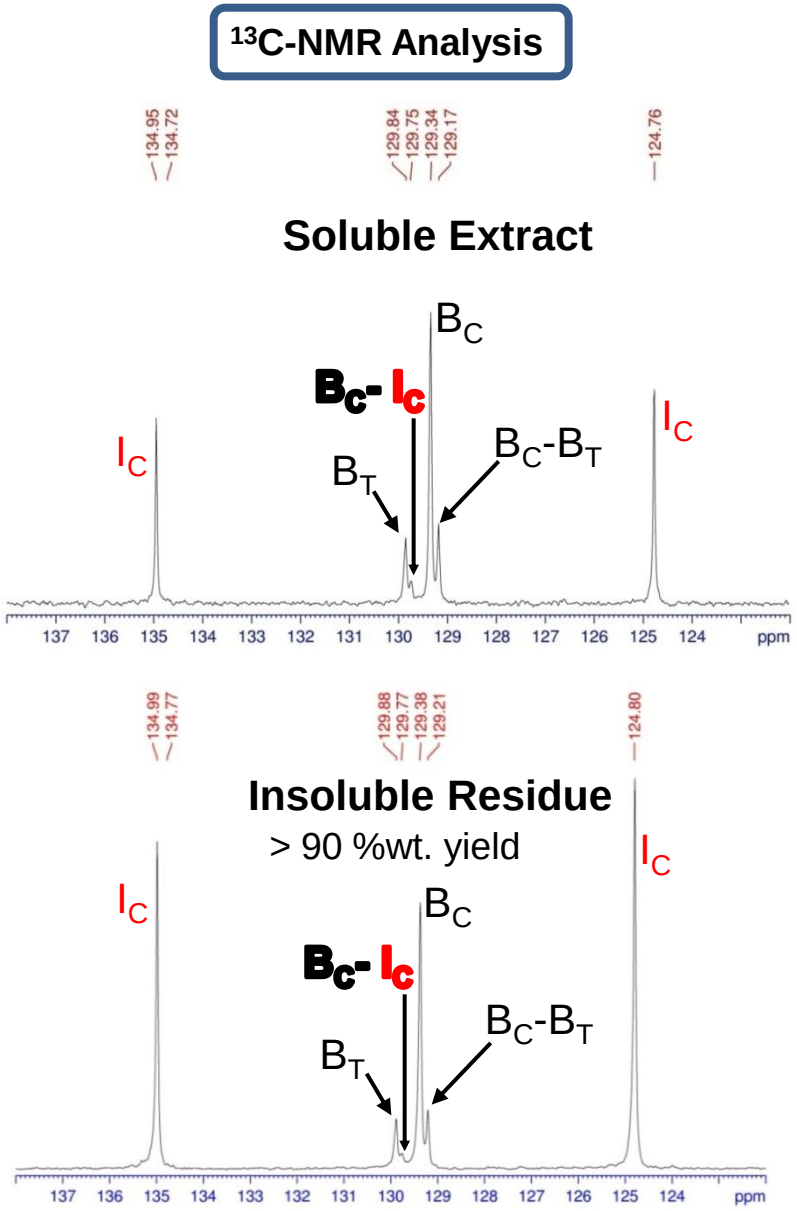
> 90 %wt. yield

K. Matsuzaki, T. Uryu, T. Asakura. *Japan Scientific Societies Press*, pp. 41–50, **1996**

Extraction in Ethyl Acetate

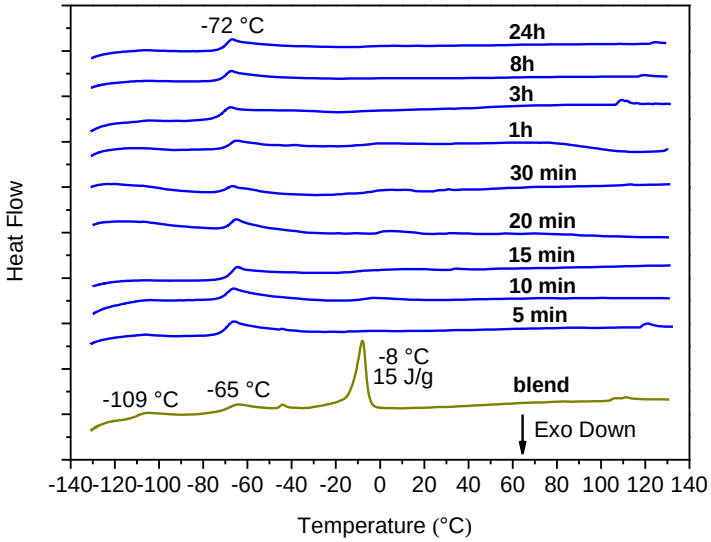




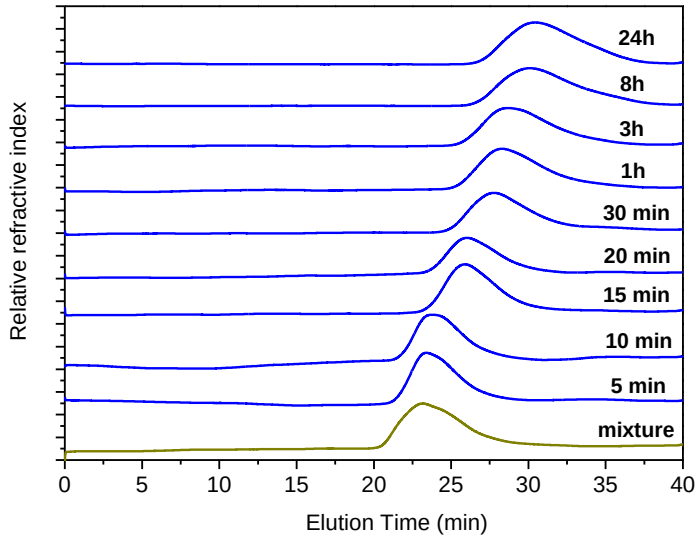


Products from 2nd Generation Catalysts

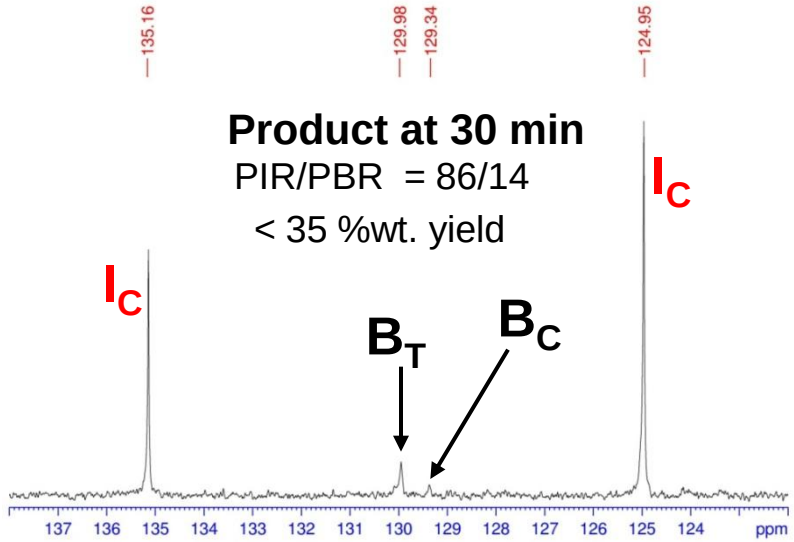
DSC Analysis

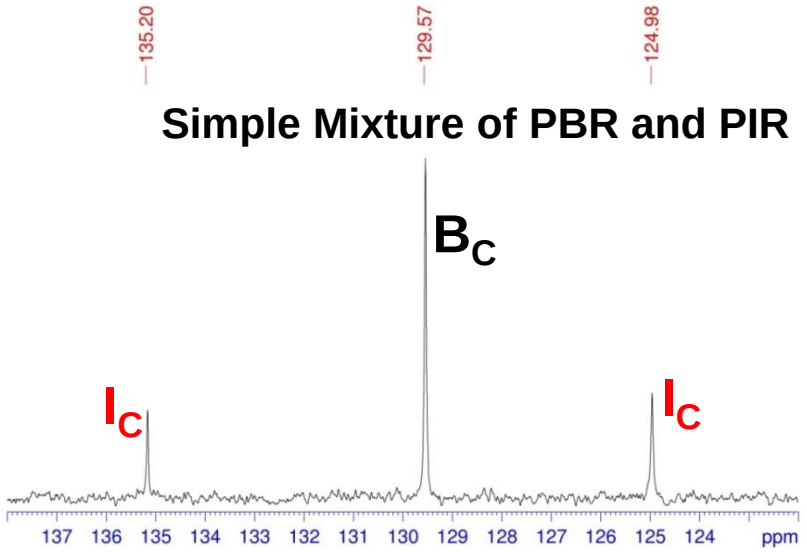


GPC Analysis



^{13}C-NMR Analysis





Conclusions

Graphite-Based Nanofillers

➢ **Tailor-made graphitic nanofillers** with different interlayer distance and different degree of crystalline order were successfully obtained.

Rubber Nanocomposites

➢ **The intercalation of GO** with long-chain guests improves the compatibility of GO with rubbers.

➢ GOICs **remarkably affect the mechanical and thermal properties** of the derived rubber nanocomposites.

Macromolecular Cross-Metathesis of Rubbers

➢ Metathesis reactions were used to prepare **innovative polymer-polymer materials**.

➢ **High-*cis* random multiblock PBR-PIR copolymers** were preferentially obtained with 1st generation metathesis catalysts.

➢ **Degradation of rubbers** was preferentially obtained by 2nd generation metathesis catalysts.

Acknowledgements

Prof. Gaetano Guerra

Prof. Pasquale Longo

Dr. Simona Longo
Dr. M. Rosaria Acocella
Dr. Christophe Daniel
Dr. Annaluisa Mariconda
Dr. Mario Maggio
Dr. Simona Daniele
Dr. Sheila Ortega Sanchez

Prof. Maurizio Galimberti

Dr. Valeria Cipolletti

Dr. Sara Musto

Dr. Vineet Kumar

Dr. Lucia Conzatti

Dr. Pellegrino Musto

Dr. Pietro La Manna

Dr. Luca Giannini

Dr. Thomas Hanel

Dr. Angela Lostritto

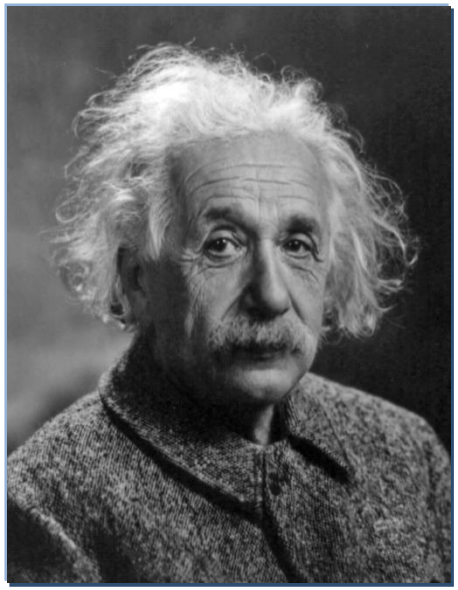
Publications

1. L. Giannini, A. Lostritto, V.Cipolletti, M. Mauro, P. Longo, G. Guerra. *Appl. Clay Sci., 71*, 27–31, **2013**.
2. M. Mauro, V. Cipolletti, M. Galimberti, P. Longo, G. Guerra. *J. Phys. Chem. C*, *116*, 24809–24813, **2012**.
3. P. Russo, B. Vetrano, D. Acierno, M. Mauro. *Polym. Compos.*, *34***,** 1460–1470, **2013**.
4. M. Mauro, M. Maggio, V. Cipolletti, M. Galimberti, P. Longo, G. Guerra. *Carbon*, *61*, 395–403, **2013**.
5. M. Galimberti, V. Cipolletti, M. Mauro, L. Conzatti. *Macromol. Chem. Phys.*, *214*, 1931–1939, **2013**.
6. S. Longo, M. Mauro, C. Daniel, M. Galimberti, G. Guerra. *Front. Chem.*, *1*, 1–9, **2013**.
7. V. Cipolletti, M. Galimberti, M. Mauro, G. Guerra. *Appl. Clay Sci.*, *87,* 179–188, **2014**.
8. M. R. Acocella, M. Mauro, L. Falivene, L. Cavallo, G. Guerra. *ACS Catalysis*, *4*, 492–496, **2014**.
9. M. Mauro, M. R. Acocella, C. Esposito Corcione, A. Maffezzoli, G. Guerra. Submitted for publication to *Chem. Mater.*
10. S. Longo, M. Mauro, C. Daniel, P. Musto, G. Guerra. Submitted for publication to *Polymer*
11. M. Galimberti, V. Cipolletti, S. Musto, S. Cioppa, G. Peli, M. Mauro, G. Guerra, S. Agnelli, T. Riccò, V. Kumar. Submitted for publication to *Rubber Chem. Technol.*

+ 14 Contributions to International Congresses

Thanks for your kind attention

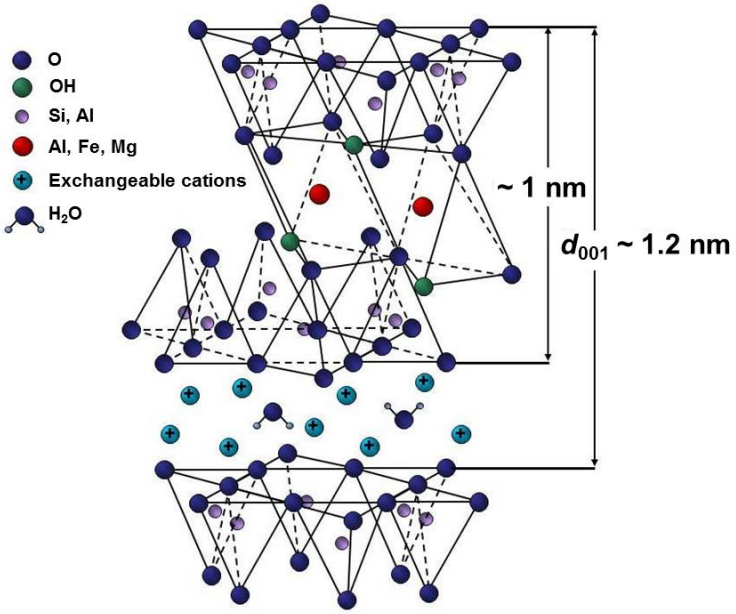
The true sign of intelligence is not knowledge but imagination.



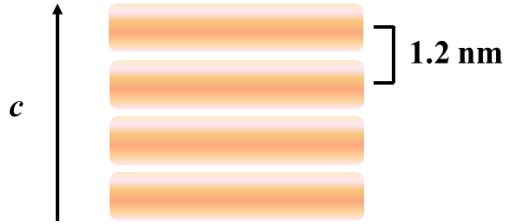
SUPPORT

Cationic Clays: Montmorillonite

Montmorillonite (MMT) is a cationic clay, made of negatively charged layers with the interlayer space filled by alkali and alkaline earth cations.

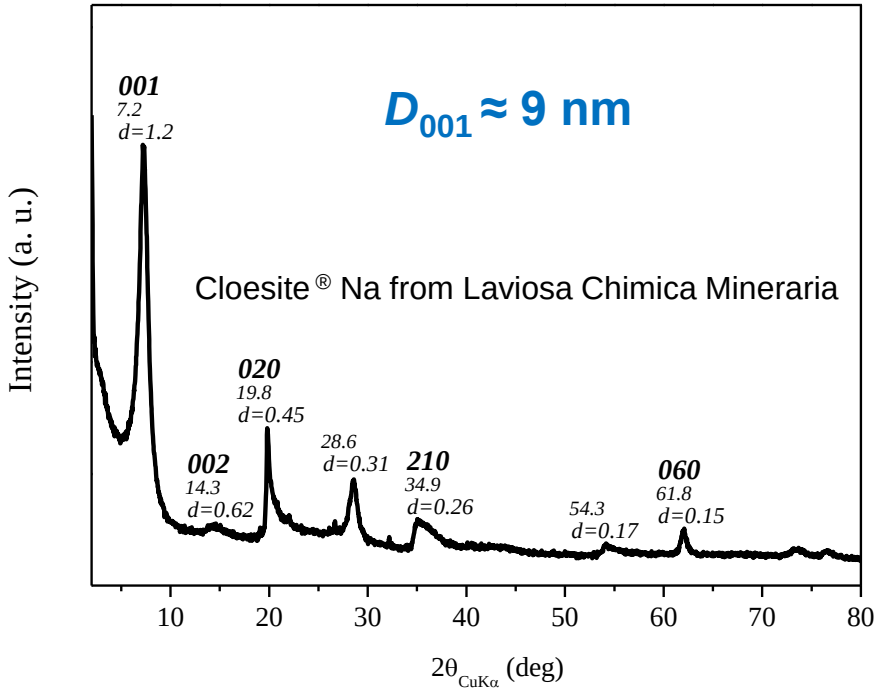


$$[(Mg_{0.33}Al_{1.67})Si_4O_{10}(OH)_2]Na_{0.33}$$



Periodicity: Bragg law $d = \lambda/2\sin\theta$

$d_{001} \approx 1.2$nm



Crystallite size: Scherrer equation

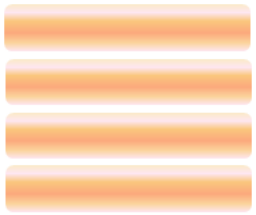
$D = K\lambda/\beta\cos\theta$

K = Scherrer Constant

λ = wavelength of radiation

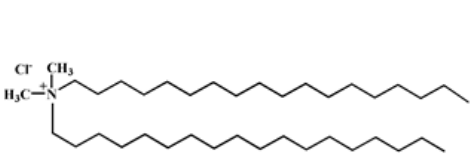
β = integral breadth

Neat Organoclays

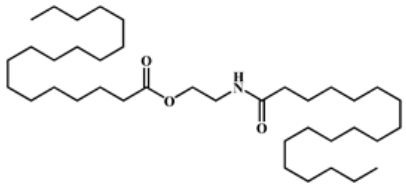


MMT: Montmorillonite

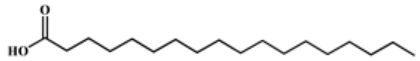
+



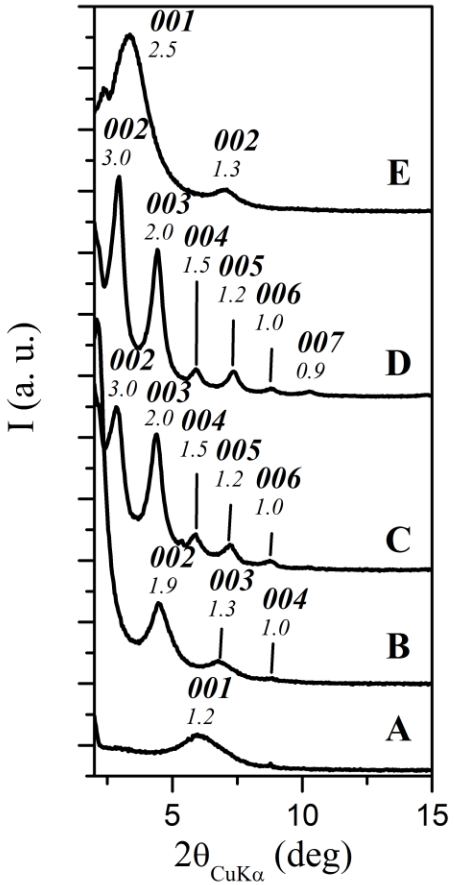
2HT: Di(hydrogenated tallow) dimethyl ammonium chloride

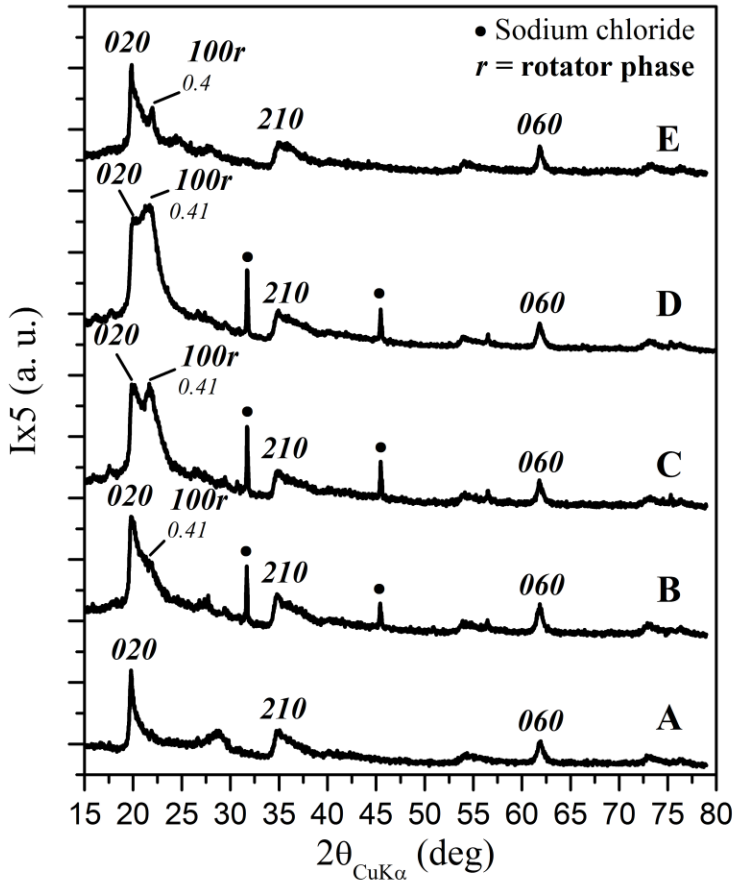


SAES: 2-stearamidoethyl stearate



SA: Stearic acid





E: B, C, D after extraction in Soxhlet with AcOEt

D: MMT+2HT+SAES

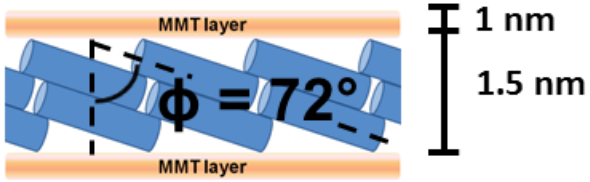
C: MMT+2HT+SA

B: MMT+2HT

A: Pristine MMT

Neat Organoclays: Structures

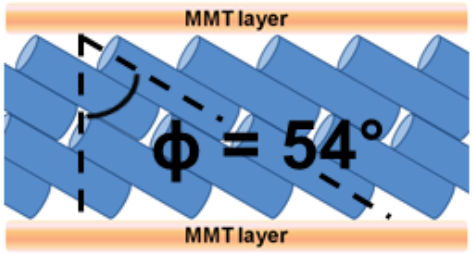
d_{001} = 2.5 nm



MMT+2HT

Tilted Bi-layer

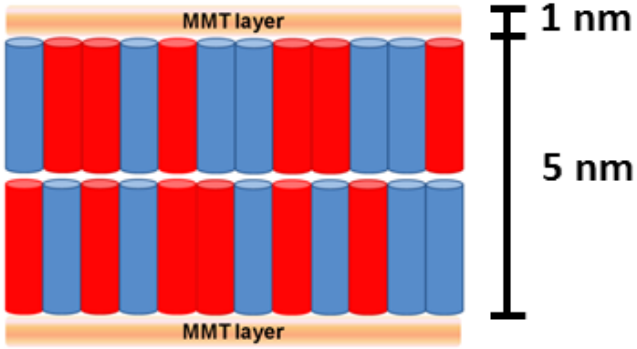
d_{001} = 4 nm



MMT+2HT

Tilted Bi-layer

d_{001} = 6 nm



MMT+2HT+SA, SAES

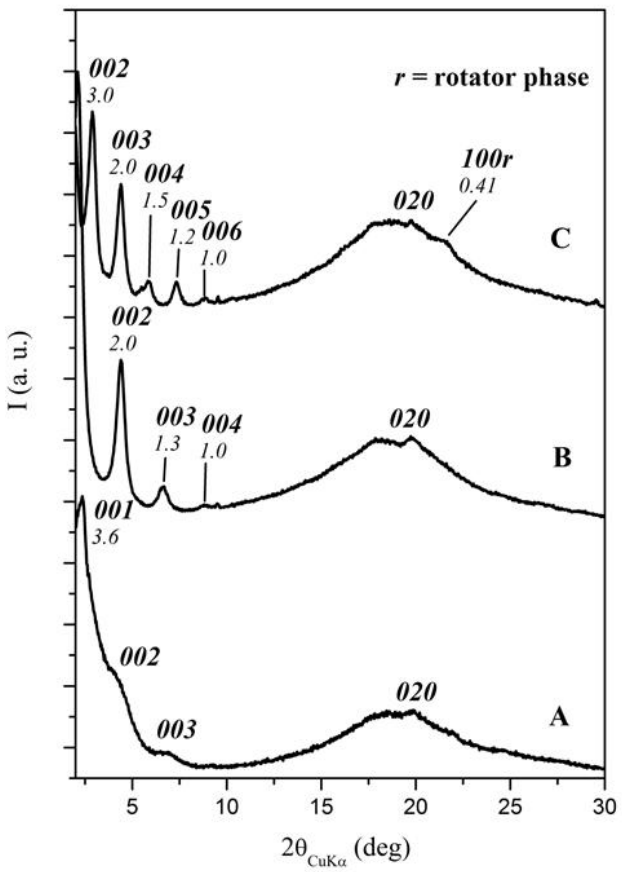
Perpendicular Bi-layer

= 2HT C18 alkyl chain

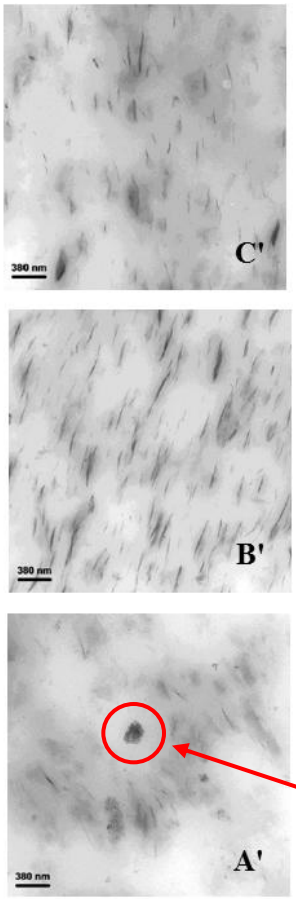
= SA, SAES C18 alkyl chain

Rubber – Organoclay Composites

Organoclays (OCs) and isoprene rubber (PIR) were melt blended in an internal mixer (PIR 100; OCs 12 phr).



TEM analysis



C, C': PIR+Mt+2HT+SA (OC with 6 nm)

Evenly distributed and finely dispersed tactoids

B, B': PIR+Mt+2HT (OC with 4 nm)

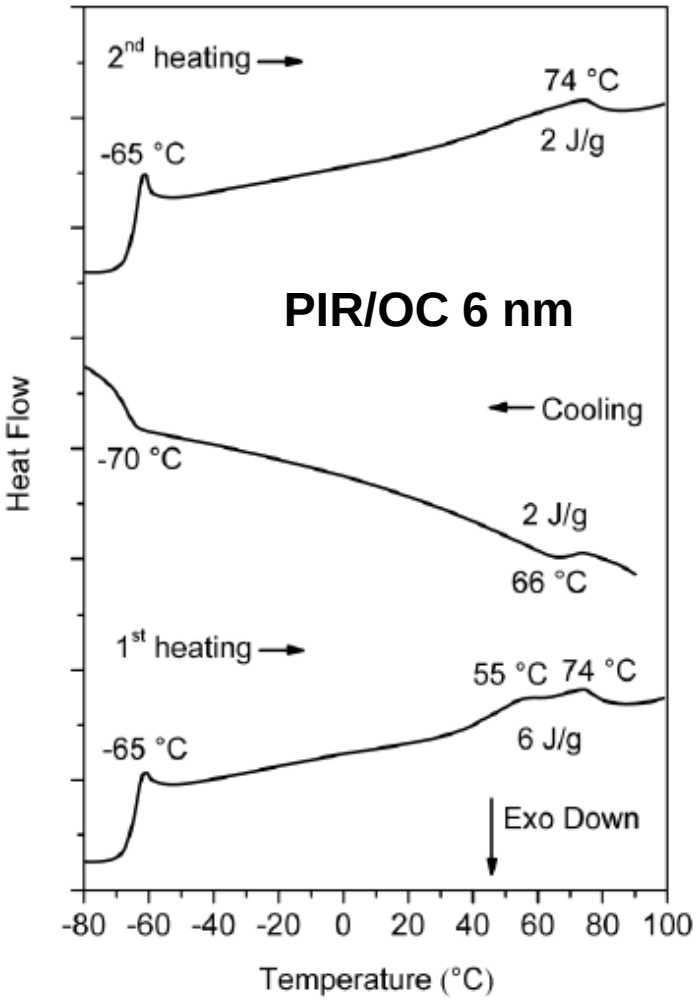
A, A': PIR+Mt+2HT (OC with 2.5 nm)

worse OCs dispersion

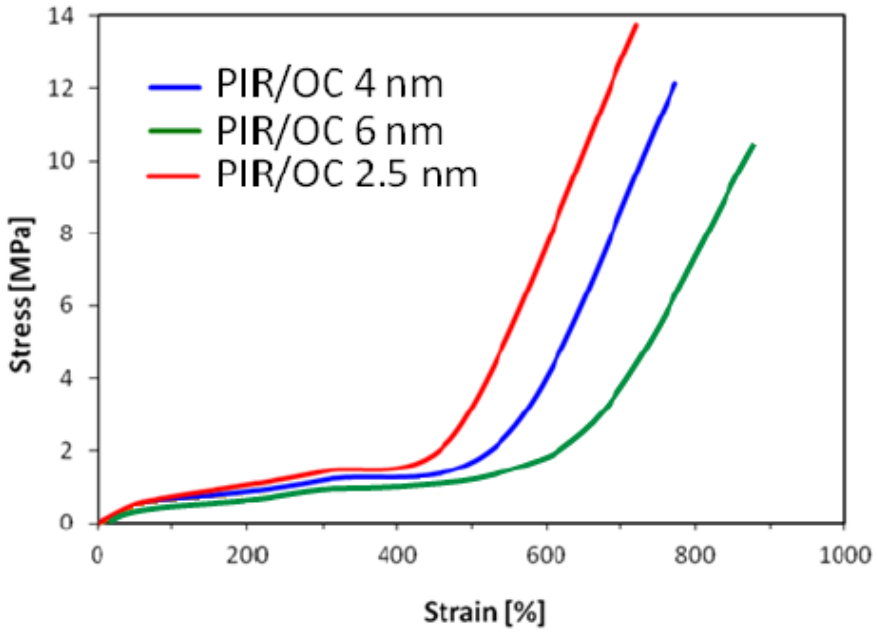
V. Cipolletti, M. Galimberti, M. Mauro, G. Guerra. *Appl. Clay Sci.*, *87,* 179–188, **2014.**

Rubber Nanocomposites Properties

DSC Analysis



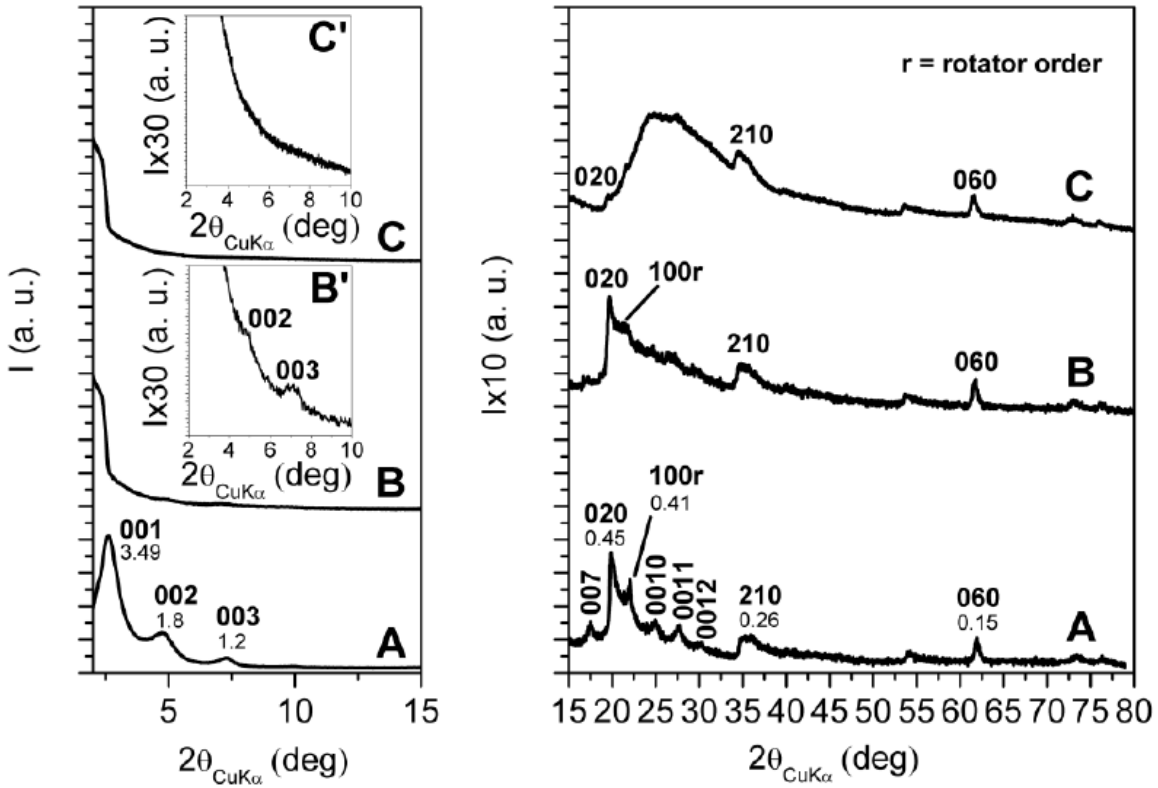
Stress-Strain Analysis



Plasticizing Effect of the Ammonium Salt

M. Galimberti, M. Coombs, V. Cipolletti, V. Kumar, M. Mauro, G. Guerra, L. Giannini. *Proceedings at the Fall 182nd Technical Meeting, Rubber Division of American Chemical Society, Cincinnati, OH (USA), October* 9-11, **2012**.

Clay Exfoliation with $scCO_2$



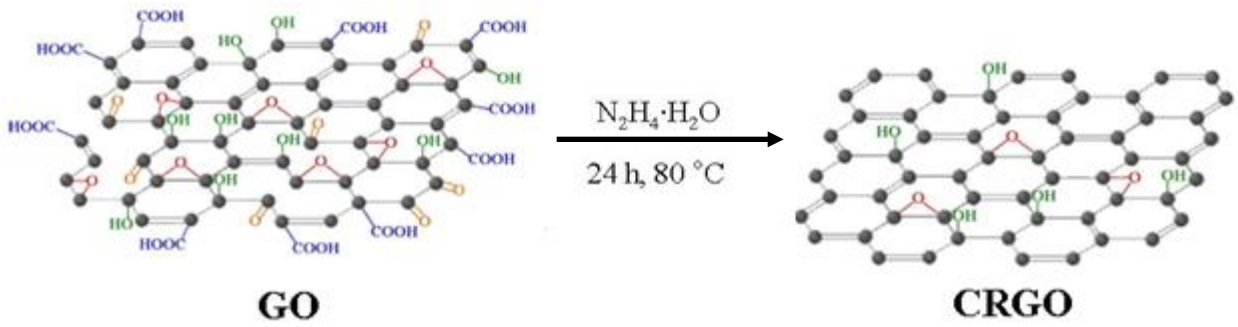
C: 16h $scCO_2$ treatment

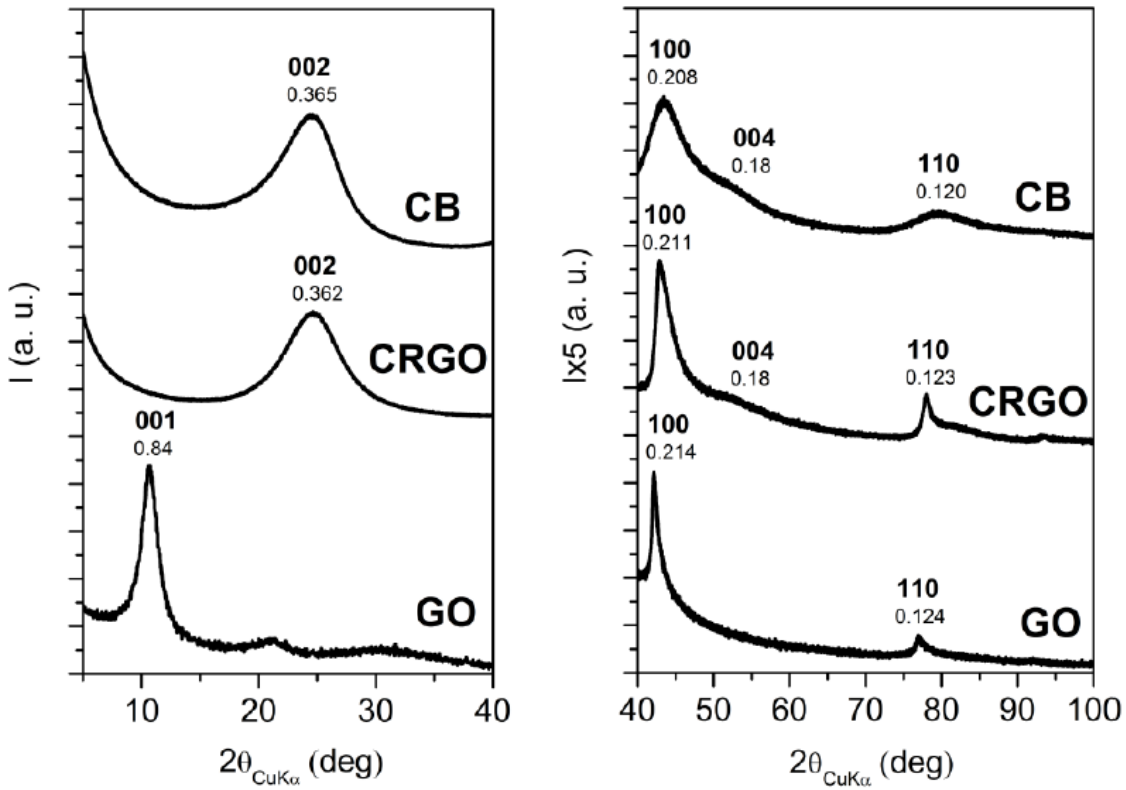
B: 16h $scCO_2$ treatment

A: Dellite® 67G

S. Longo, M. Mauro, C. Daniel, M. Galimberti, G. Guerra. *Front. Chem.*, *1*, 1–9, **2013**.

Chemically Reduced Graphite Oxide





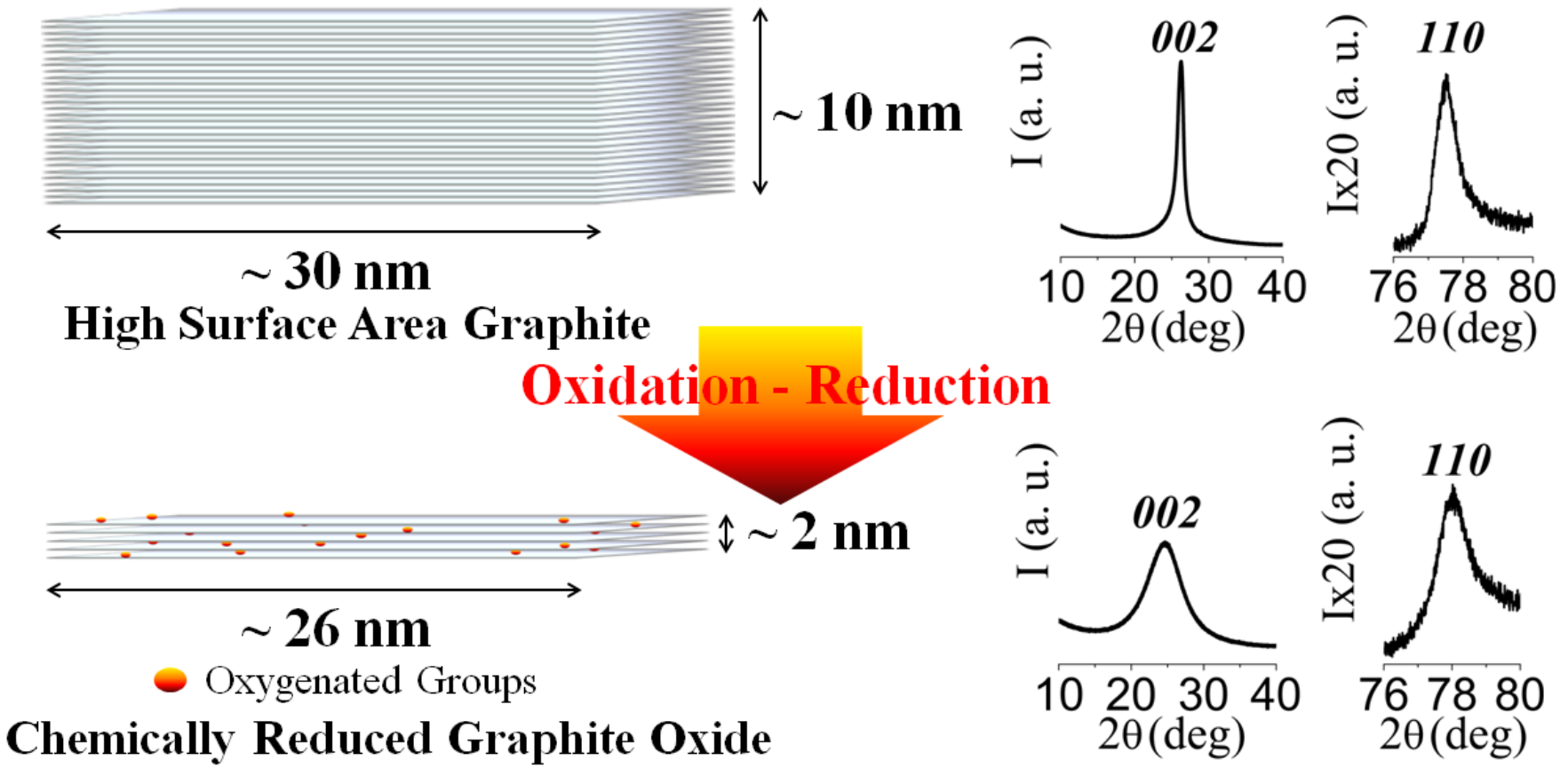
$D_{002} \approx 2$ nm $D_{110} \approx 3$ nm

$D_{002} \approx 2$ nm $D_{110} \approx 26$ nm

$D_{002} \approx 4$ nm $D_{110} \approx 30$ nm

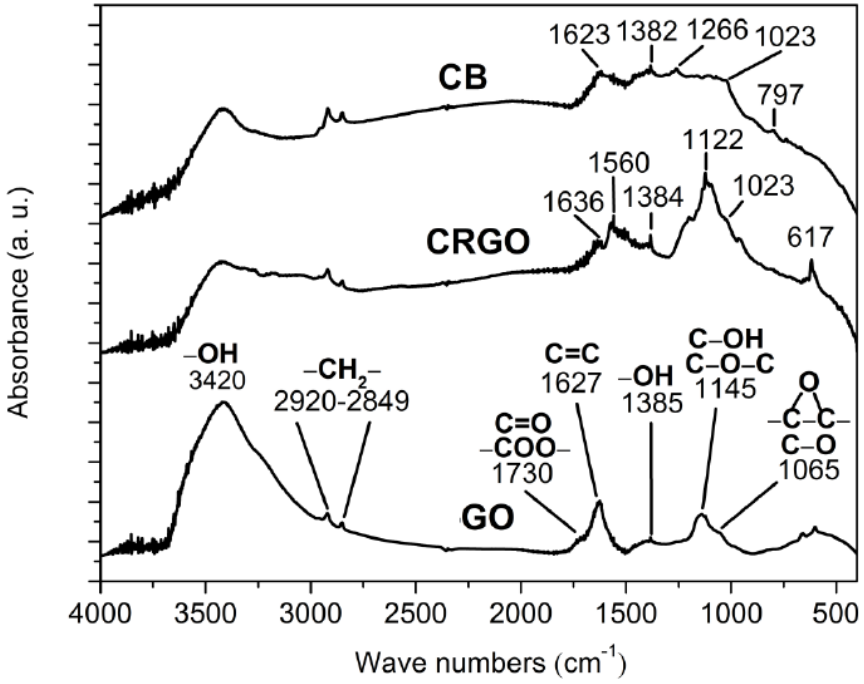
Mauro, M.; Cipolletti, V.; Galimberti M.; Longo, P.; Guerra G. *J. Phys. Chem. C.* **2012**, *116*, 24809-24813.

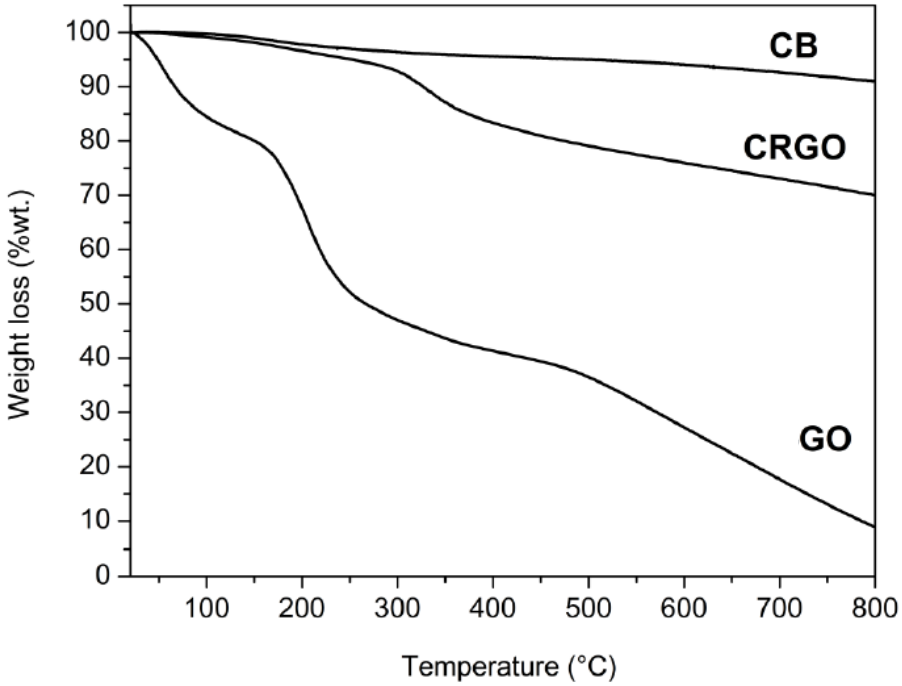
Overall Effect of Oxidation-Reduction Procedure on Graphite



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

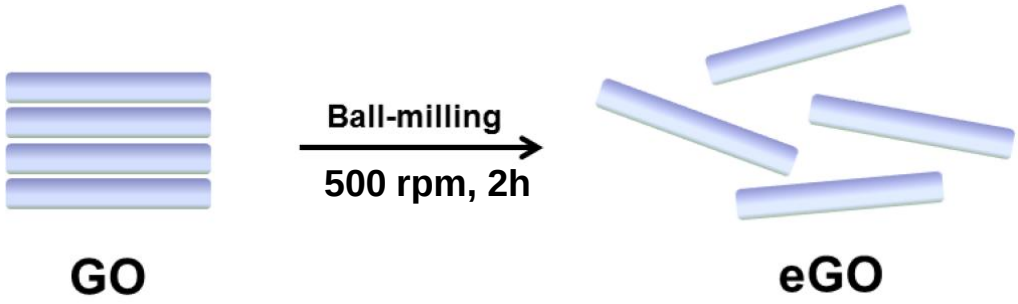
Chemically Reduced Graphite Oxide

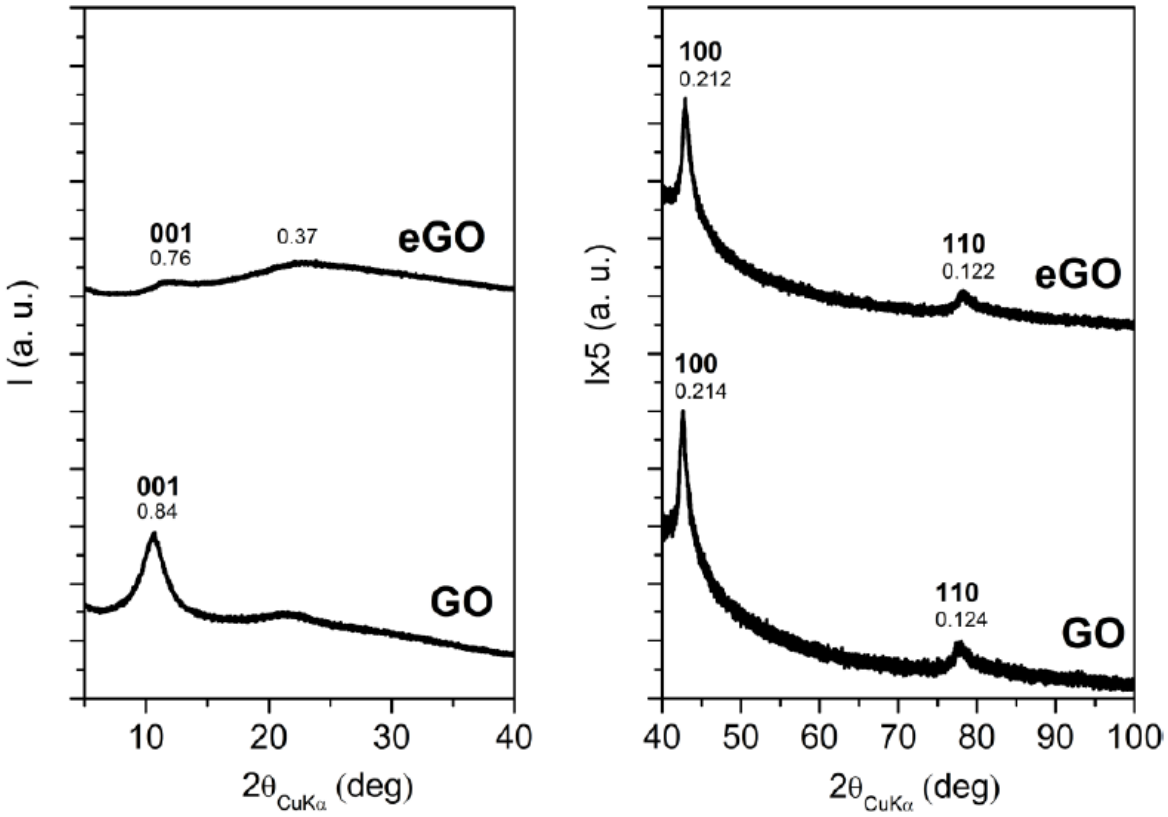


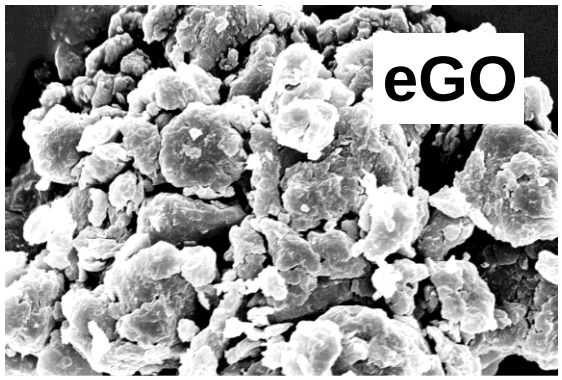


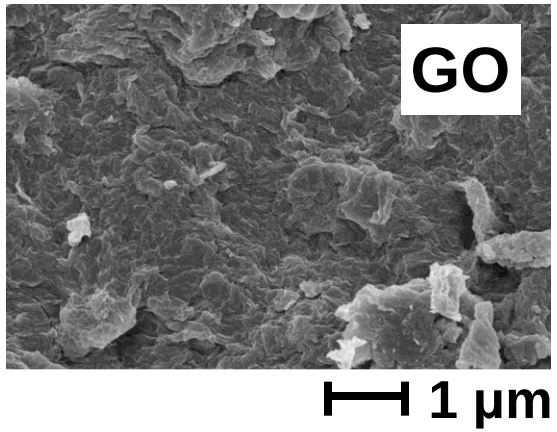
Sample	Surface area (m^2/g)	Elemental composition (%wt.)					
		C	H	N	O	S	C/O
GO	1.1	59.1	1.4	0.1	35	4.4	1.6
CRGO	46.8	79.9	0.2	2.7	17.2	0.0	4.6
CB	57.2	96.2	0.5	0.1	3.2	0.0	30.1

Mechanical Exfoliation of GO



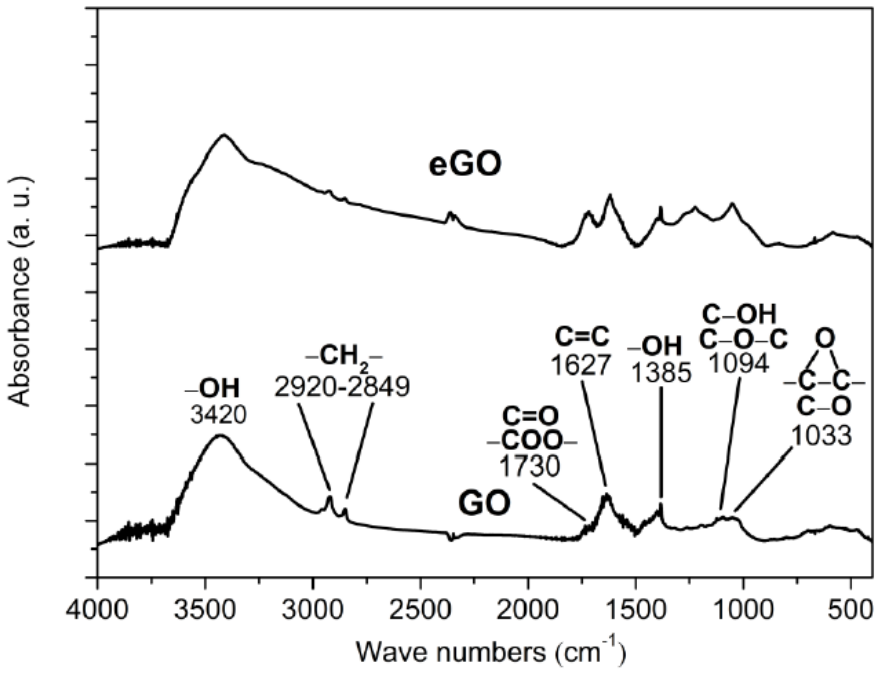


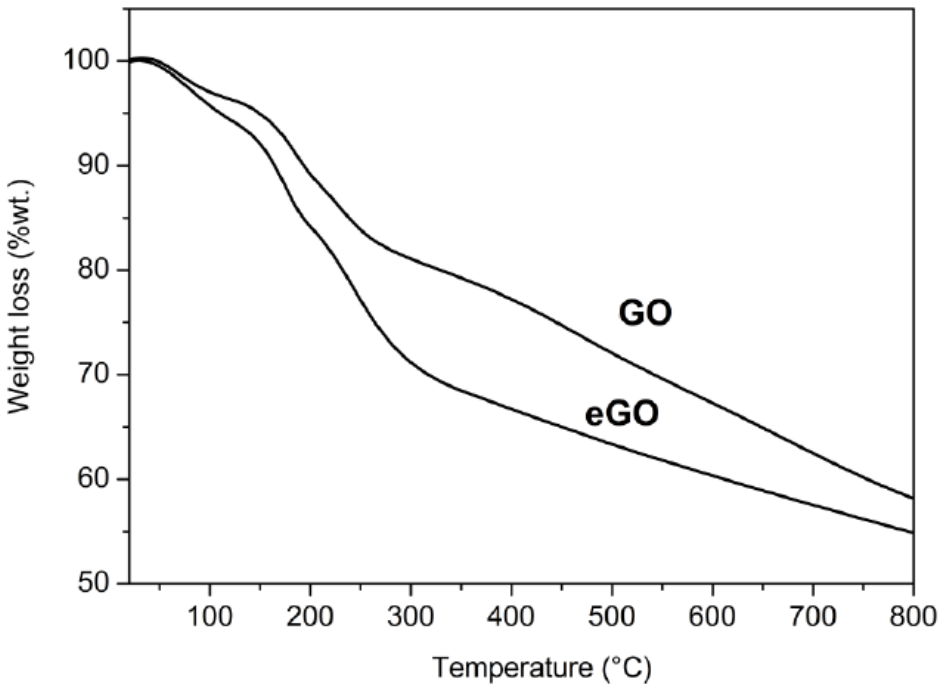




M. R. Acocella, M. Mauro, L. Falivene, L. Cavallo, G. Guerra. *ACS Catalysis*, *4*, 492–496, **2014**.

Mechanical Exfoliation of GO

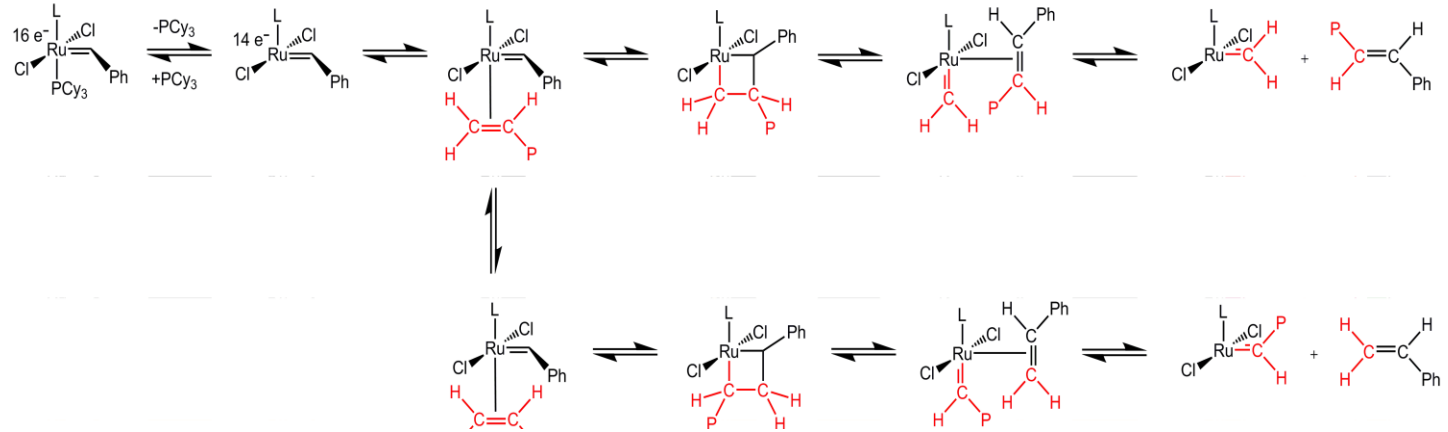




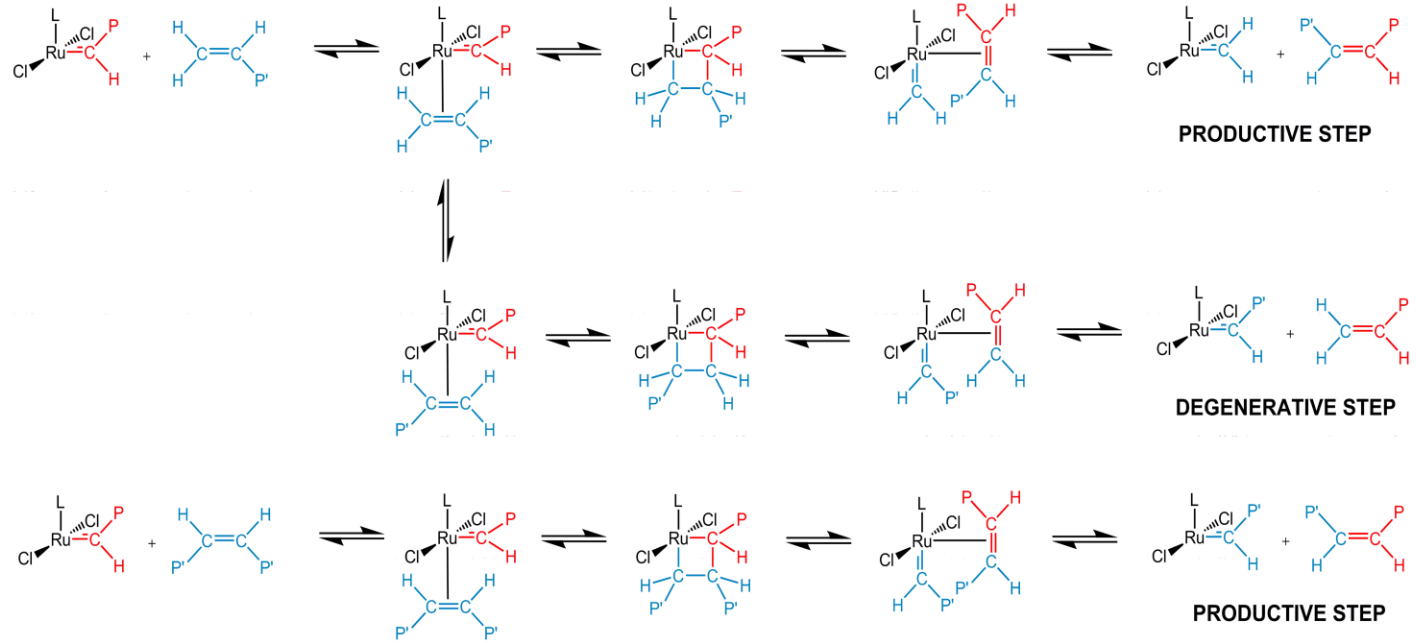
Sample	Surface area (m^2/g)	Elemental composition (%wt.)					
		C	H	N	O	S	C/O
GO	0.8	63.7	0.6	0.1	33.7	1.9	1.9
eGO	4.2	66.1	0.5	0.1	31.4	1.9	2.1

MCM Mechanism

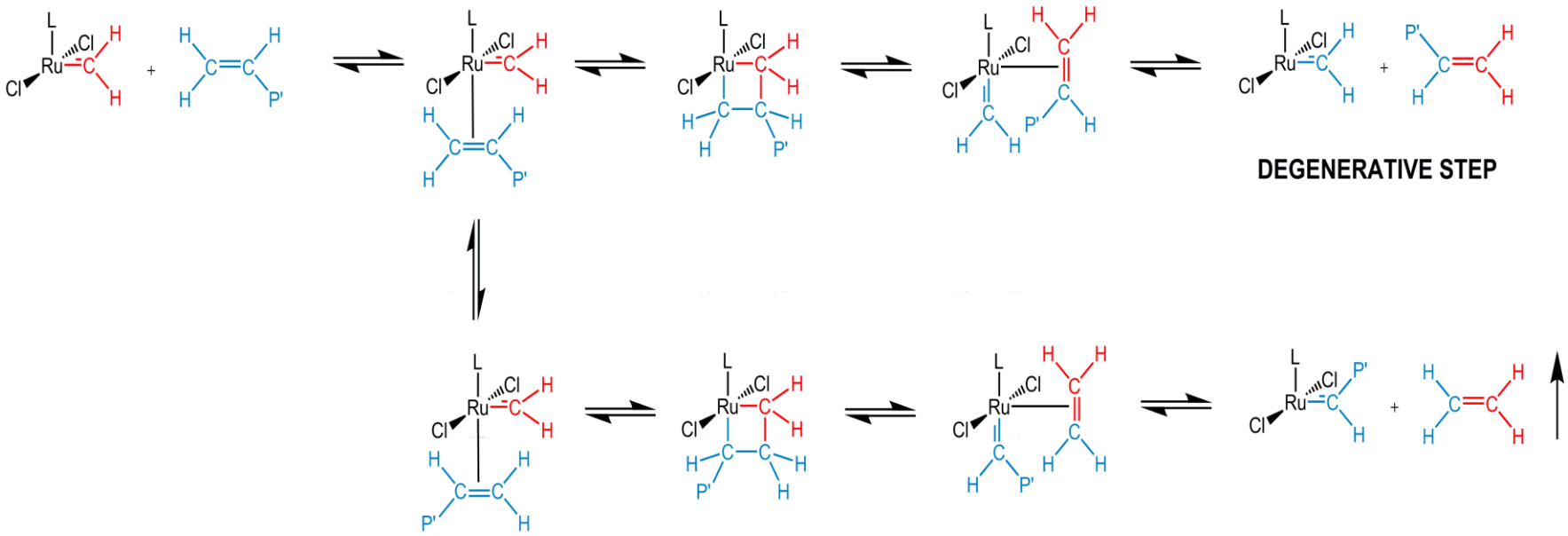
INITIATION



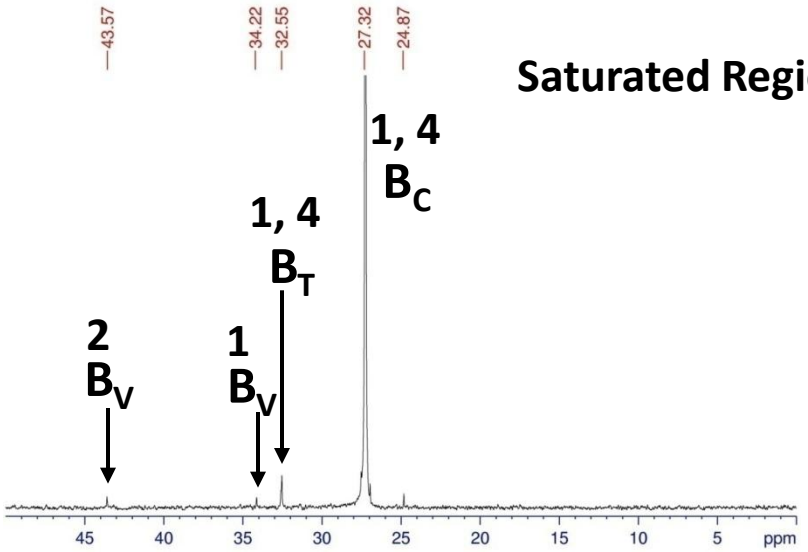
PROPAGATION

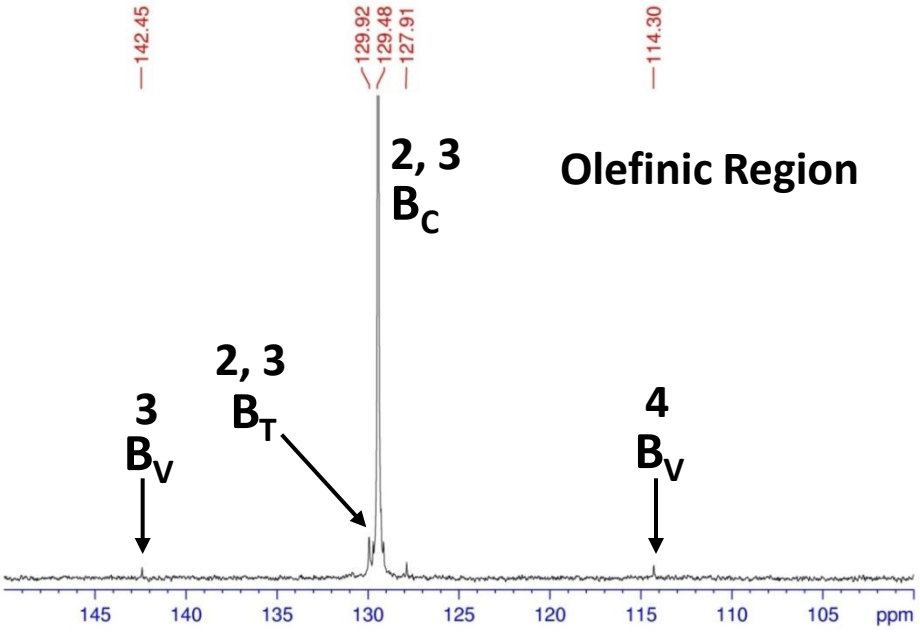


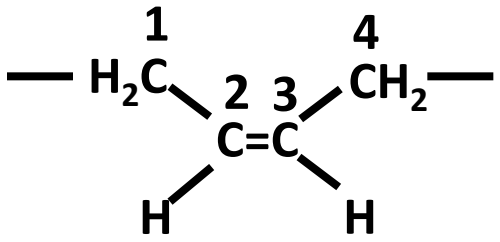
MCM Mechanism



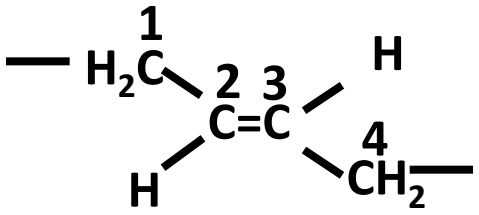
PBR NMR Characterization



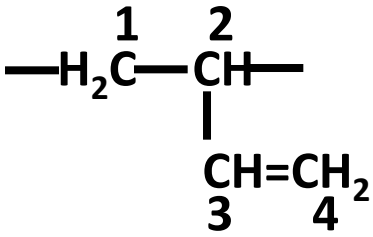




B_C : unità 1,4-*cis*-butadiene

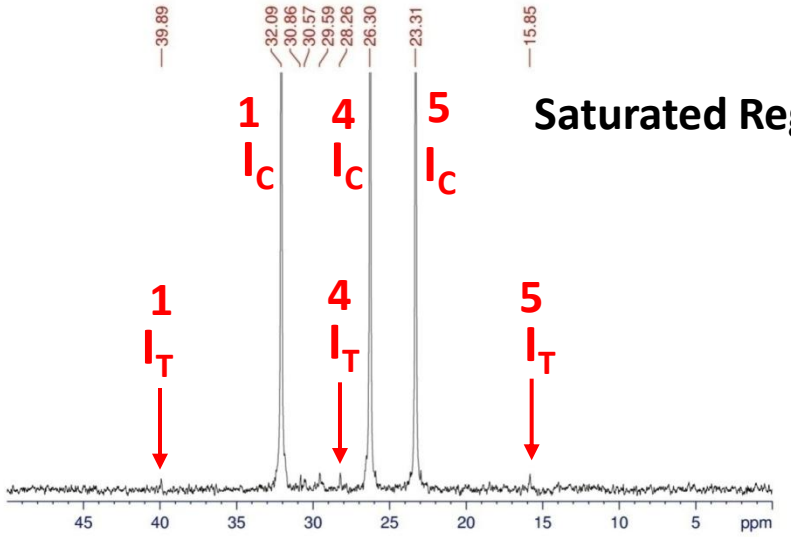


B_T : unità 1,4-*trans*-butadiene

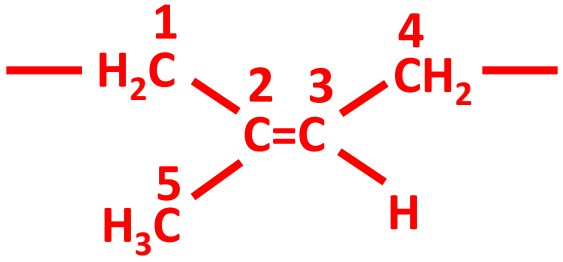


B_V : unità 1,2 butadiene

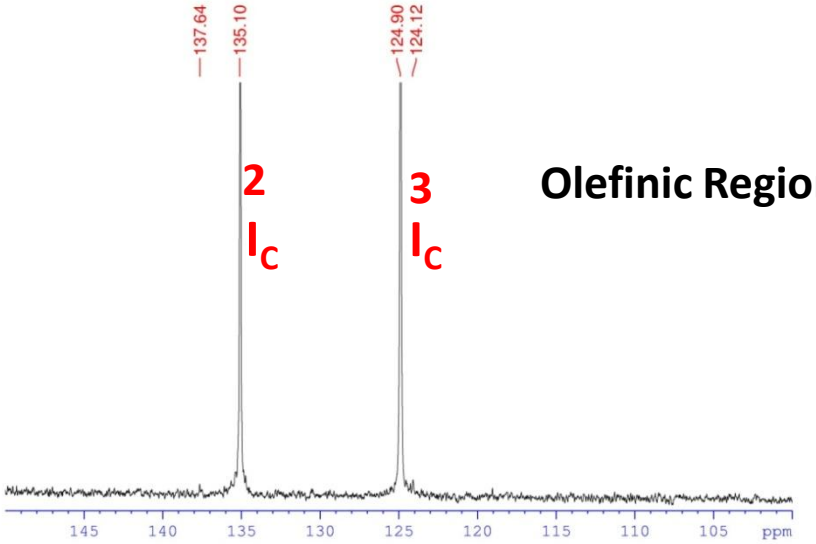
PIR NMR Characterization



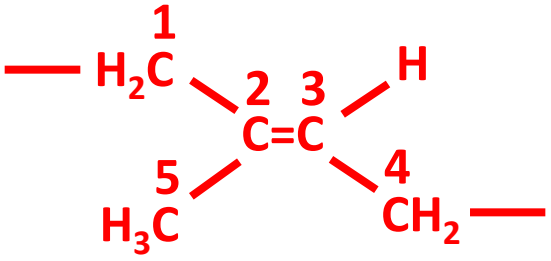
Saturated Region



I_C : unità 1,4-*cis*-isoprene



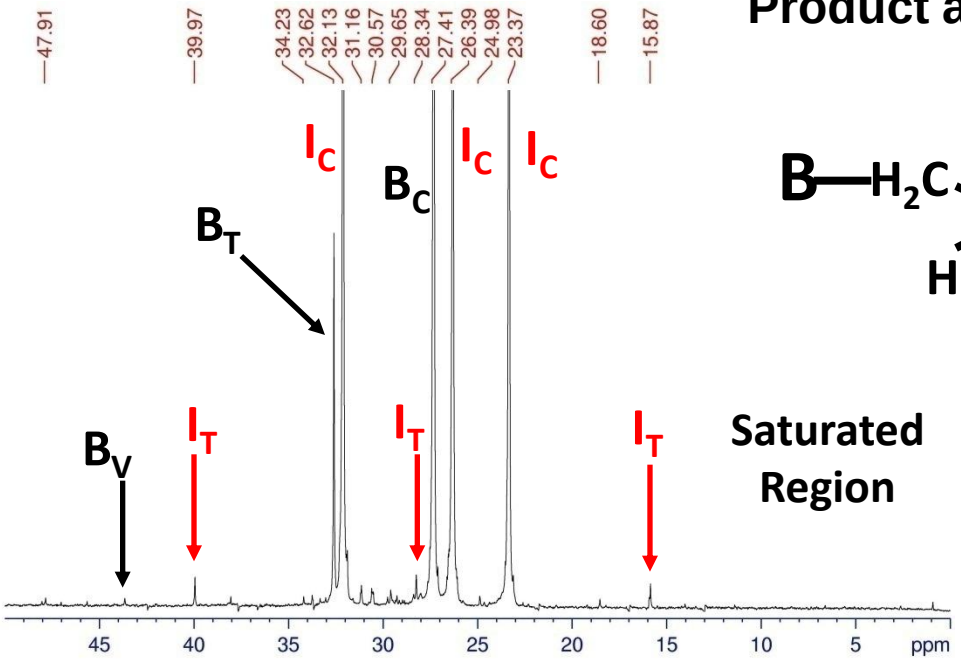
Olefinic Region



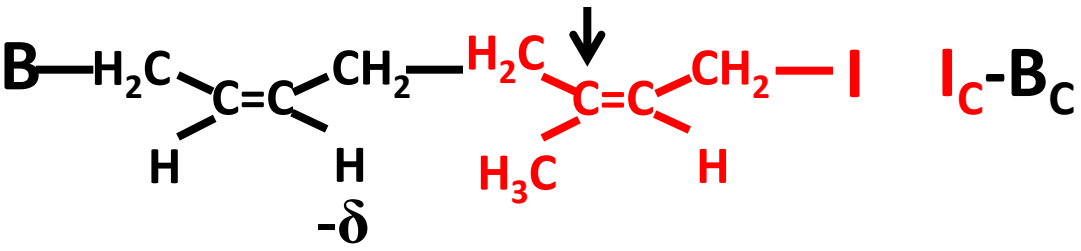
I_T : unità1,4-*trans*-isoprene

PBR-PIR NMR Characterization

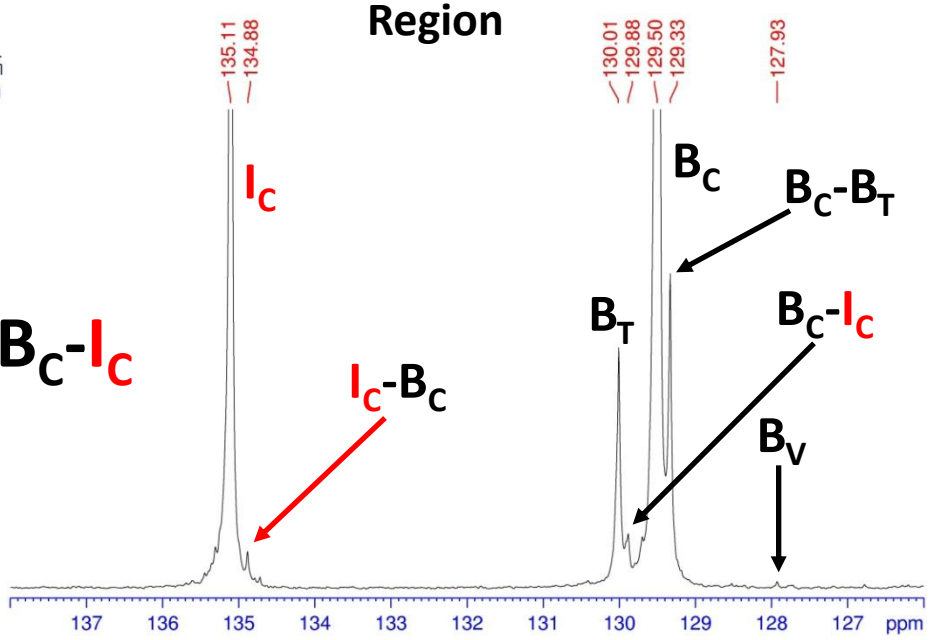
Product at 8h

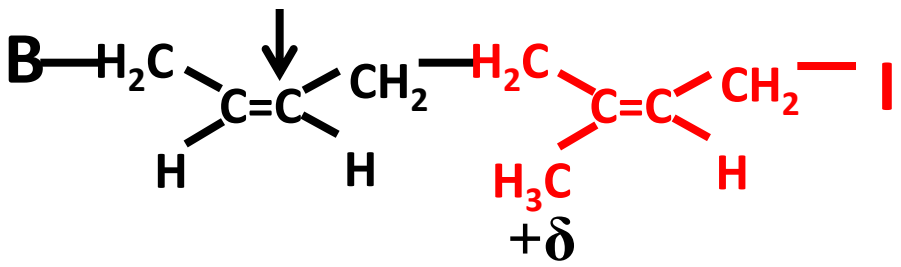


Saturated Region



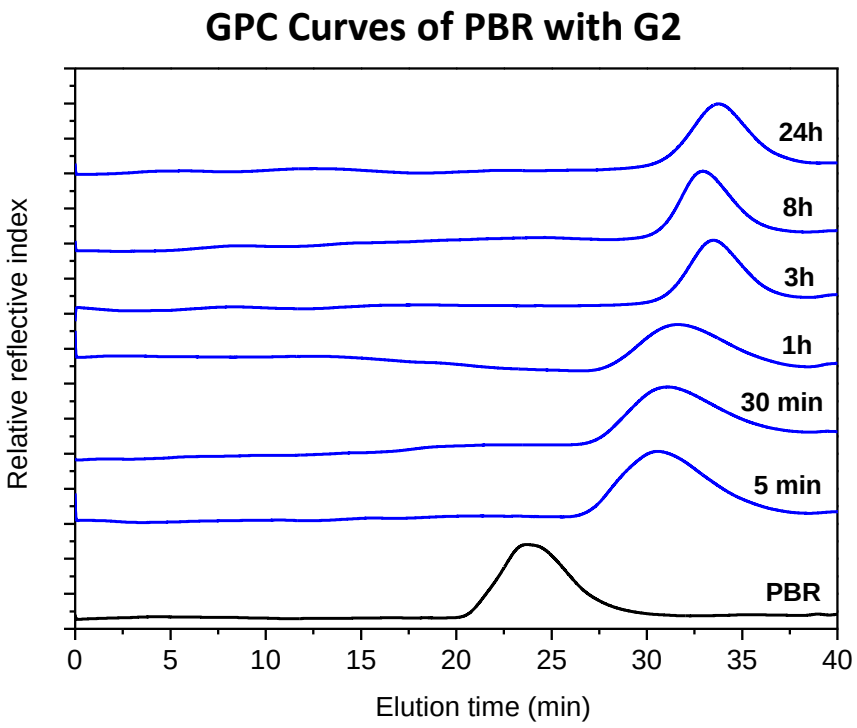
Olefinic Region

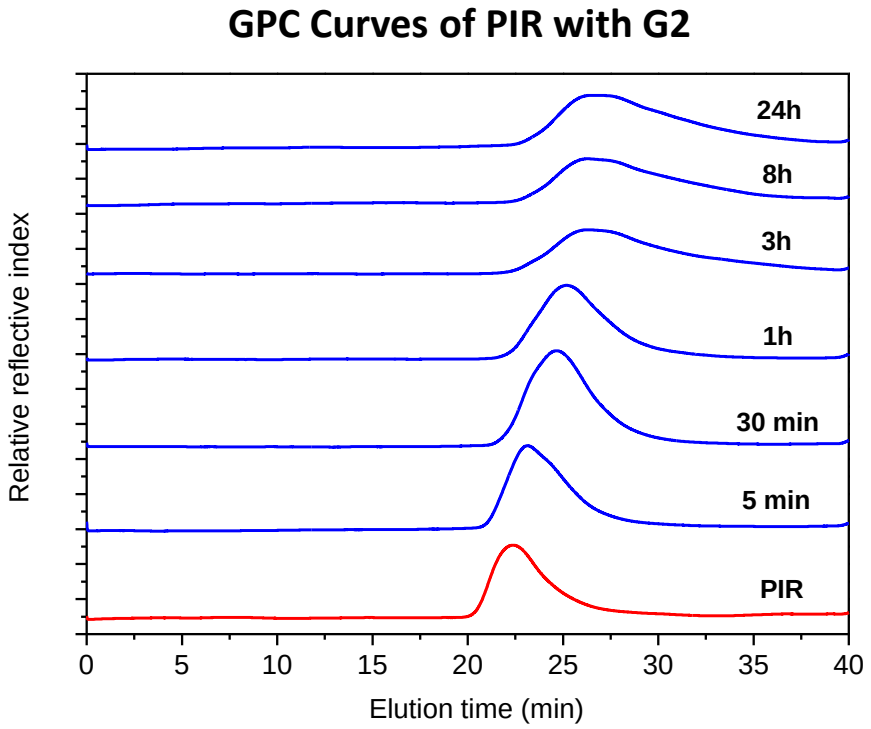




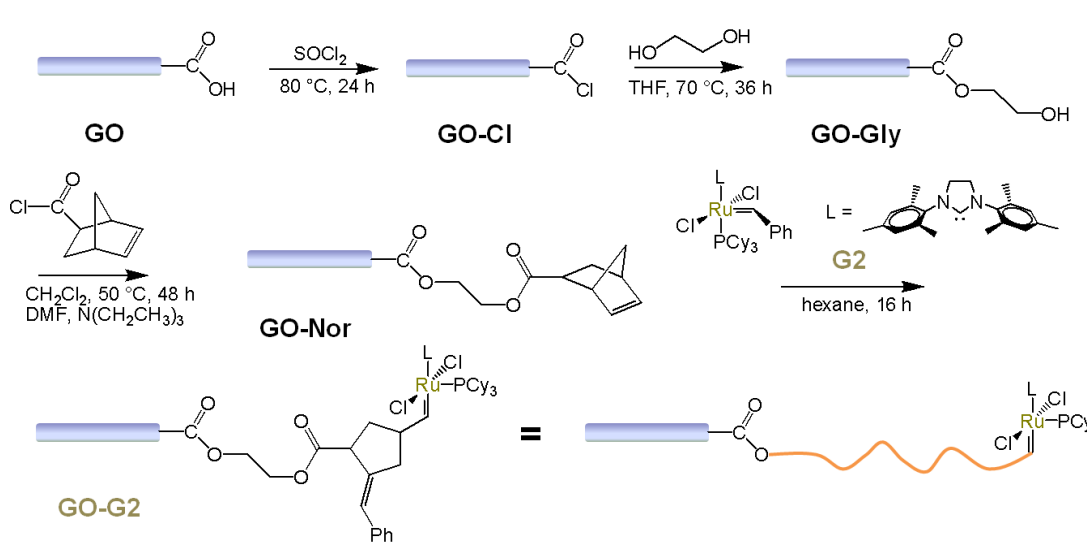
B_C-I_C

Homopolymers Degradation

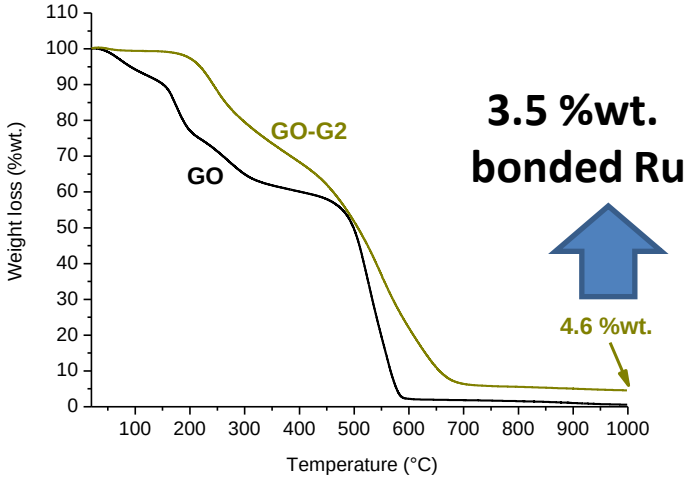




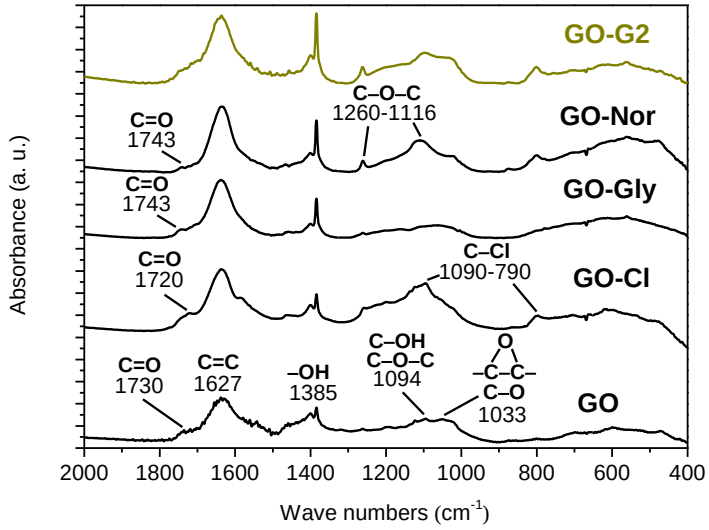
Covalent Functionalization of GO Layers



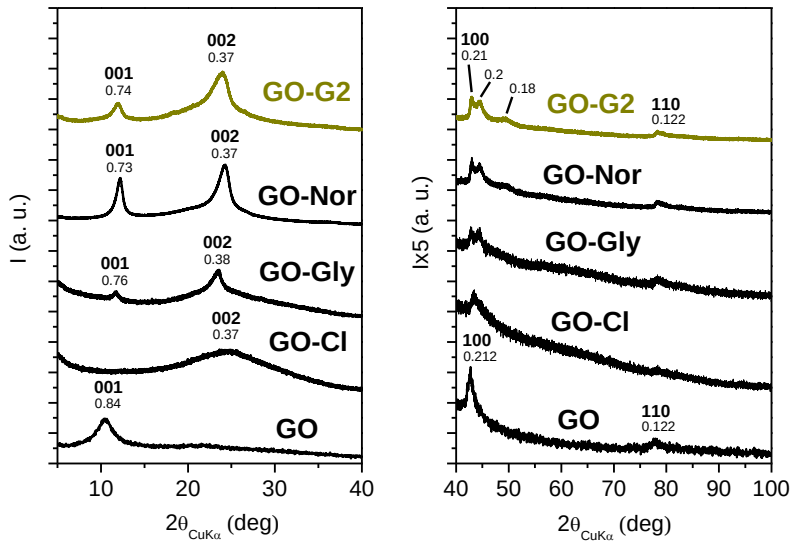
TG Analysis



FTIR Analysis

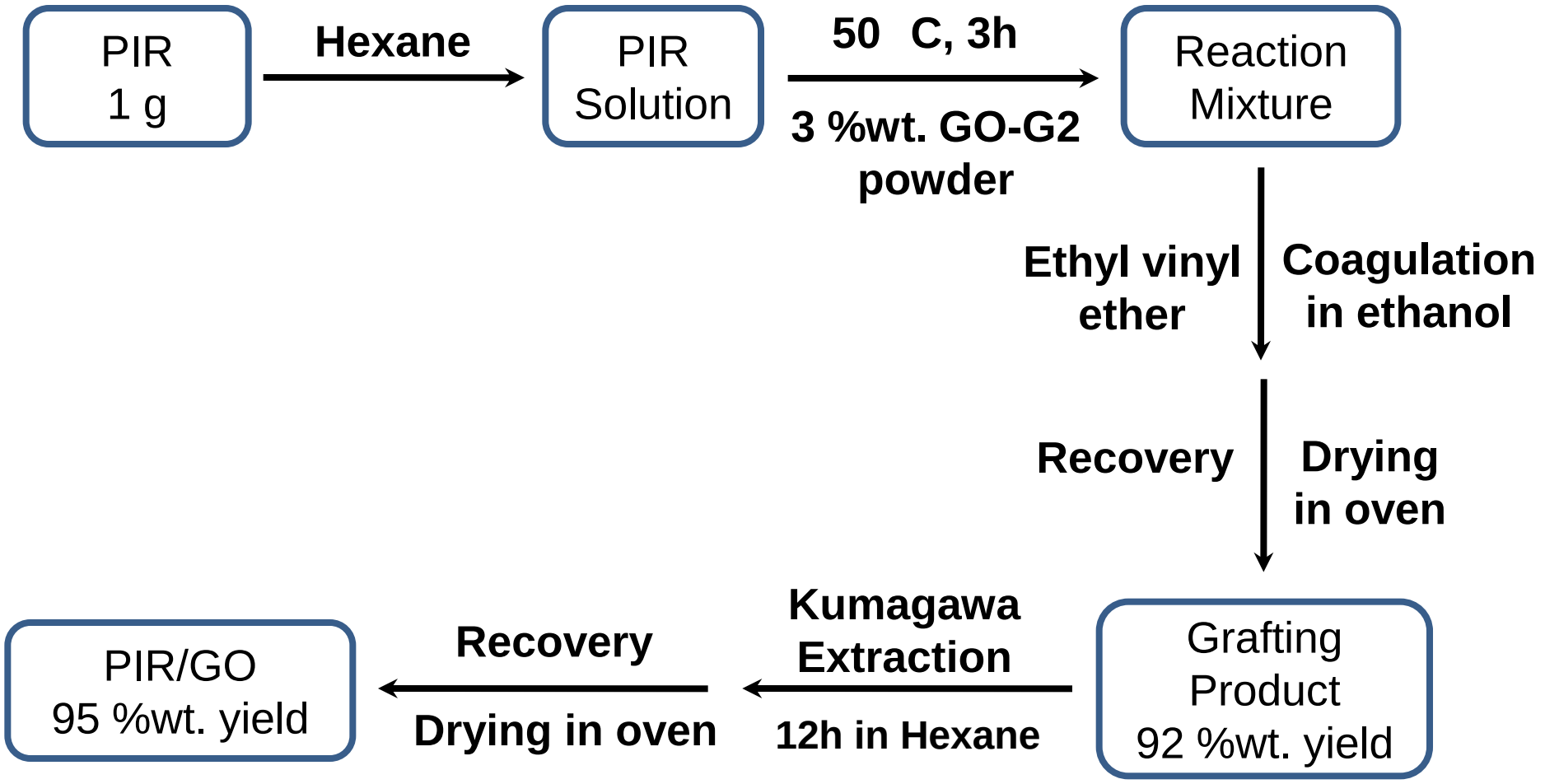


WAXD Analysis

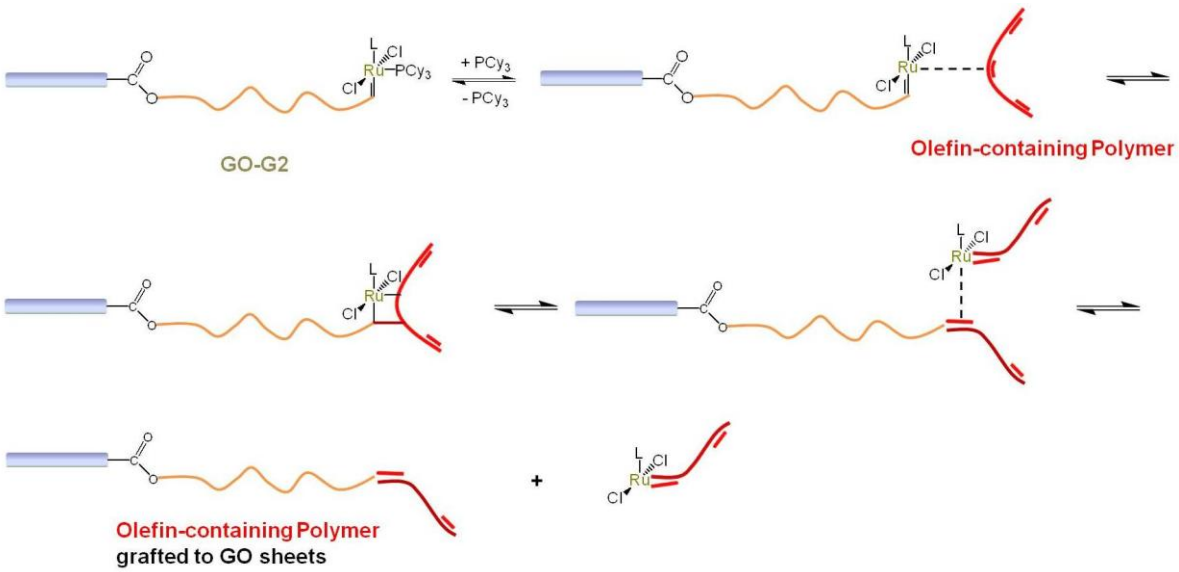


C. Costabile, F. Grisi, G. Siniscalchi, P. Longo, M. Sarno, D. Sannino, C. Leone, P. Ciambelli . J. Nanosci. Nanotech. **2011**, *11*, 1-10

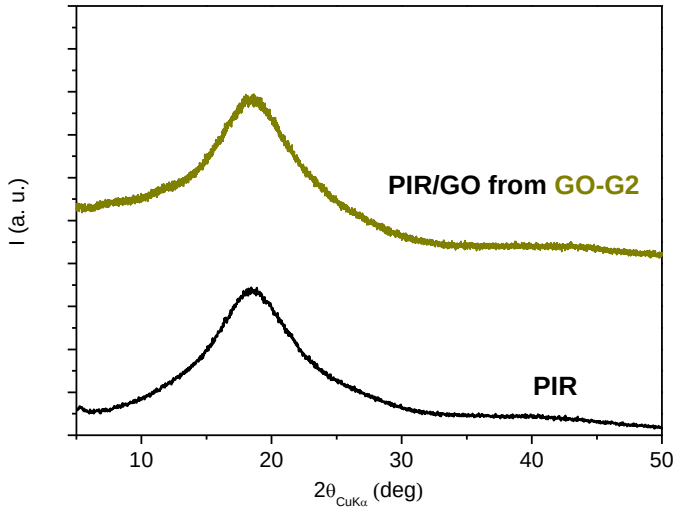
Grafting Experimental Procedure



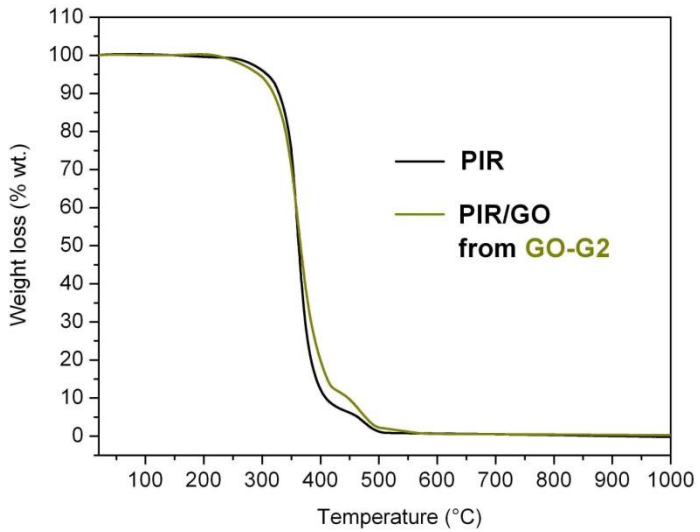
Grafting of PIR to GO Layers



WAXD Analysis



TG Analysis



DM Analysis