Integration of acrylate polymer in sol-gel silica depending on their molecular weight

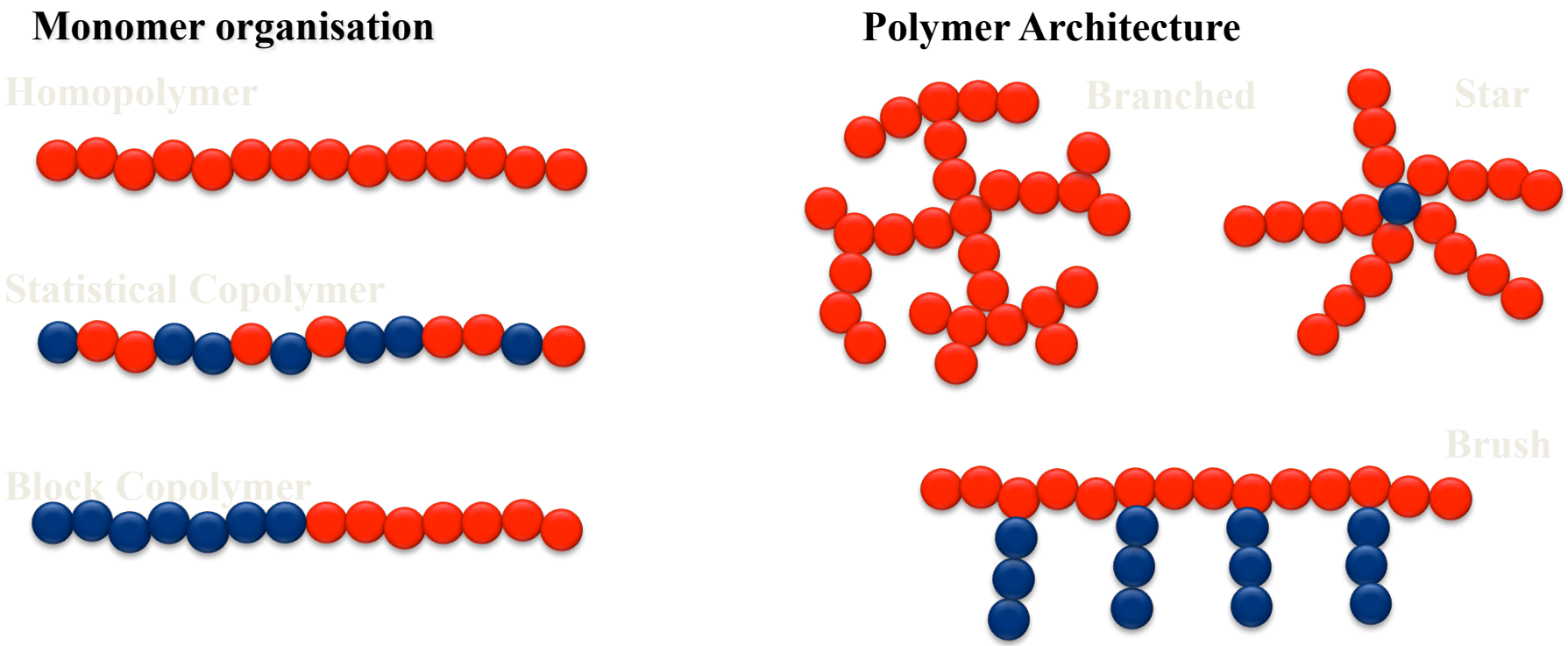
Anthony Maçon[1]

[1]Imperial College of London, UK

Confidential :)

Outline

Acrylate polymer can have different chemical properties and architecture



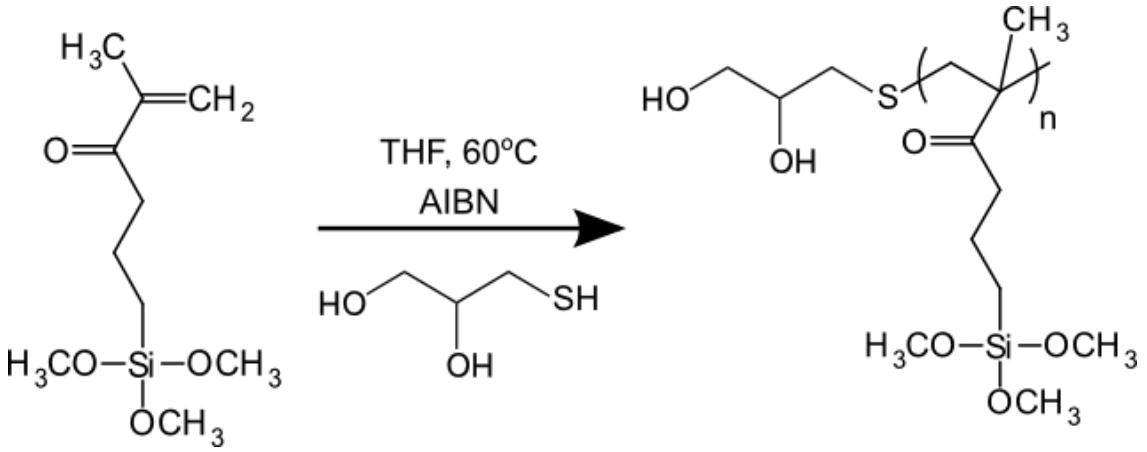
Aim & objectives

Aim

How cross linking acrylate polymers are integrated in the silica matrix depending on their molecular weight

objectives

- Use the Regulated free radical polymerization
- Characterised the polymerisation reaction
- Characterise the hybrid



Tageted M_w	$\overline{DP}_{ni}$	R_0 (x10^{-3})
30kDa	120	8.3
15kDa	60	16.6
7.5kDa	30	33.1
2.5KDa	10	99.4

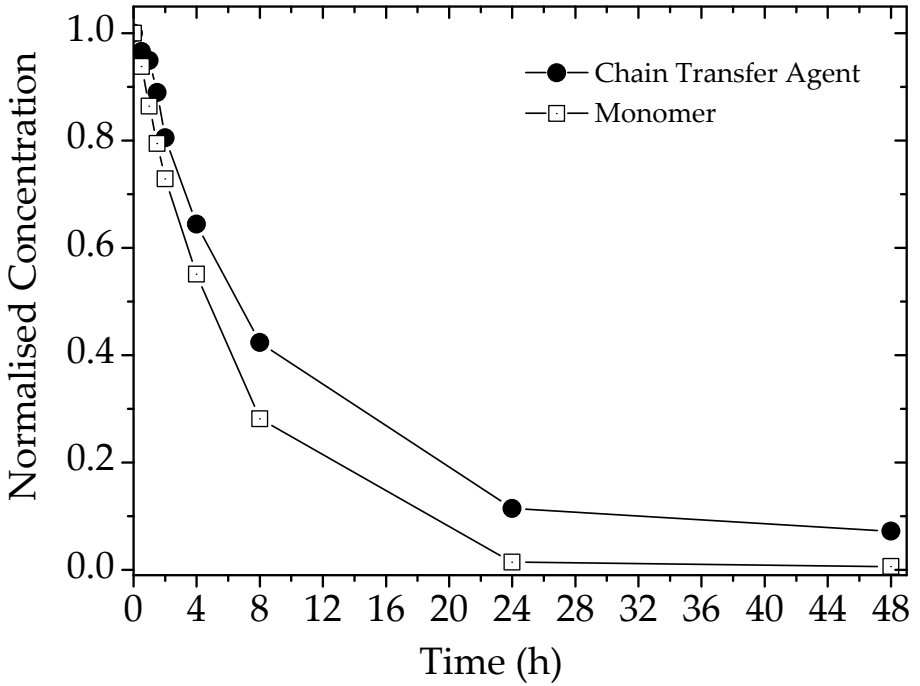
$C_{monomer} = 1 mol.L^{-1}$

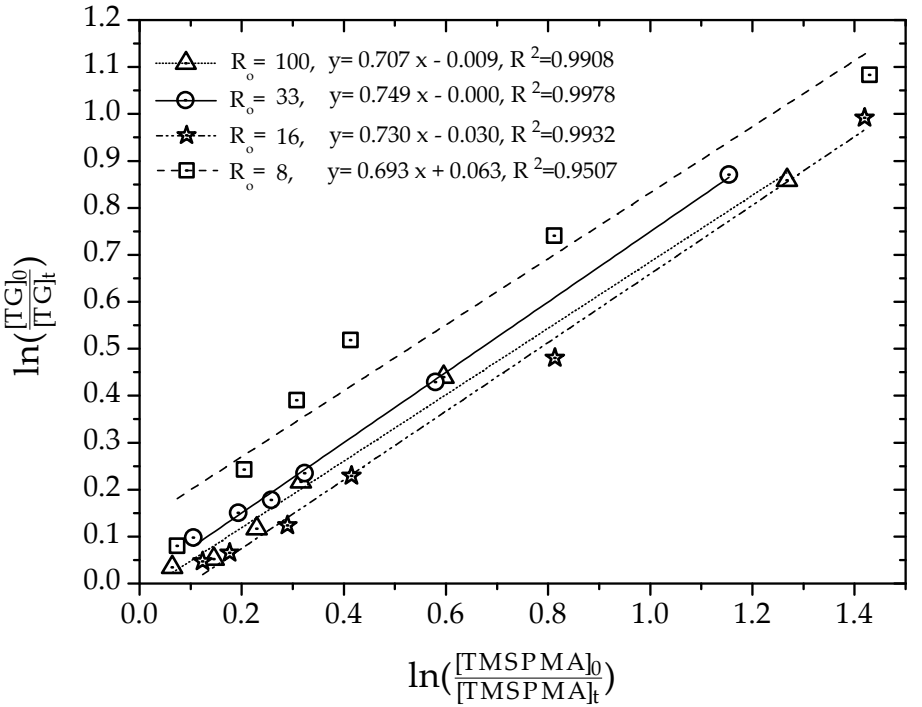
$C_0 = \frac{n_{initiator}}{n_{monomer}} = 1.5\%$

$R_0 = \frac{n_{CTA}}{n_{monomer}} = variable$

$T_0 = \frac{n_{trioxane}}{n_{monomer}} = 5\%$

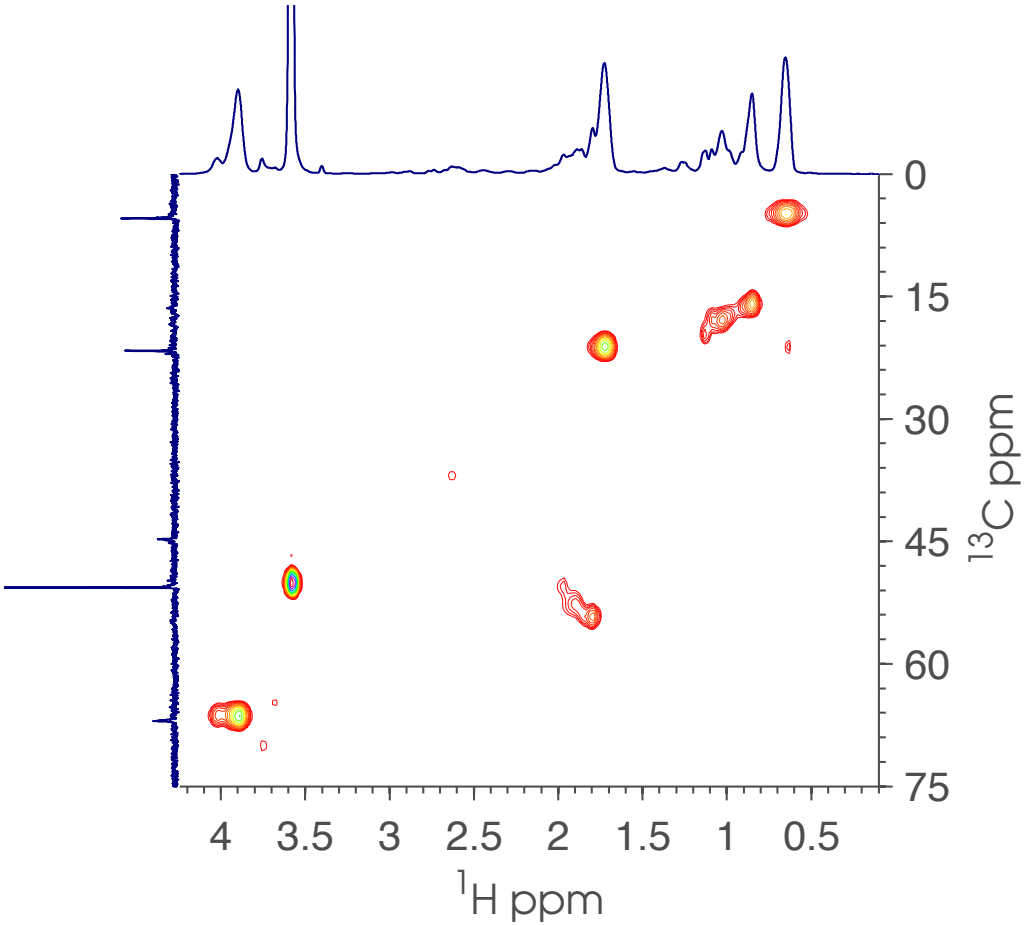
Chain Transfer constant

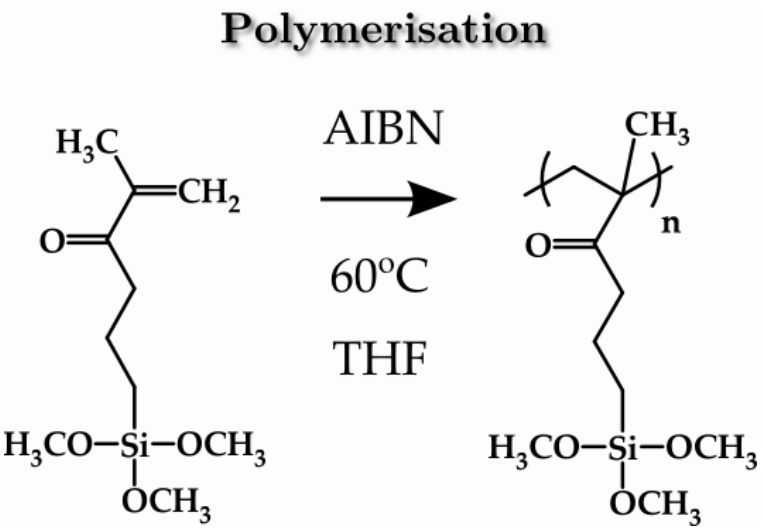




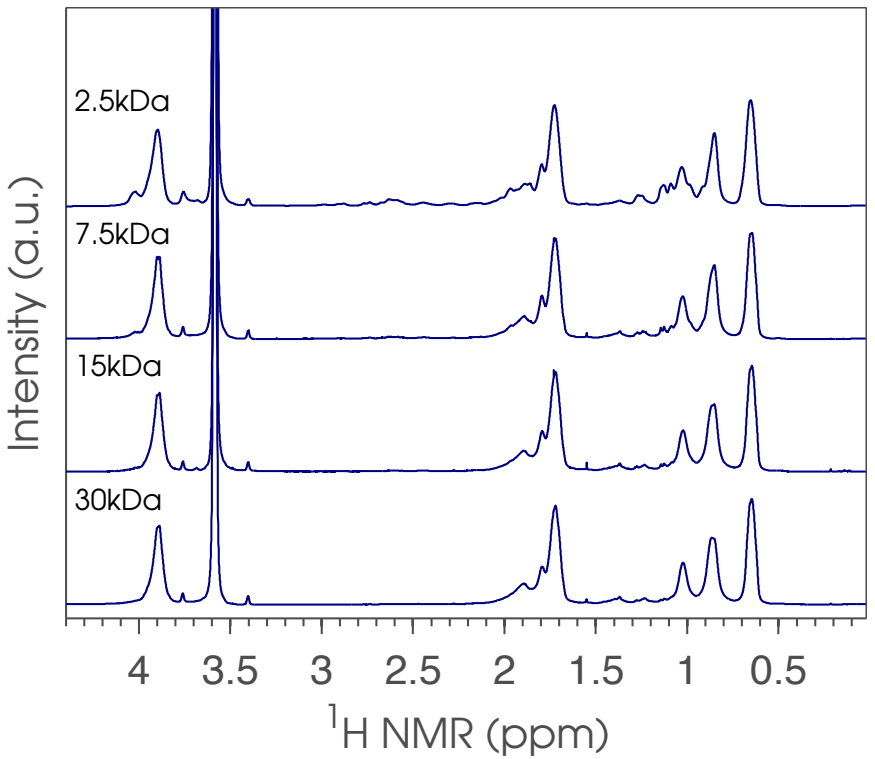
$$\left(\frac{1}{\overline{DP_n}}\right)_i = C_T \frac{[T]}{[M]} = \frac{d[T]}{d[M]}$$

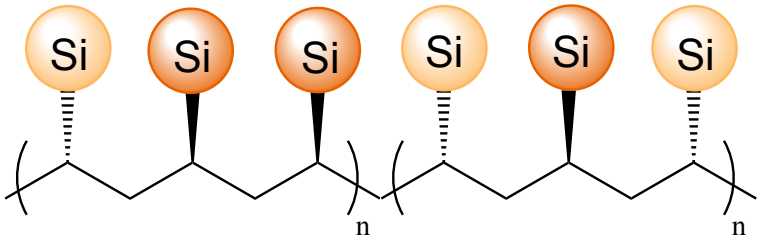
Chemical Structure : NMR





Chemical Structure : NMR



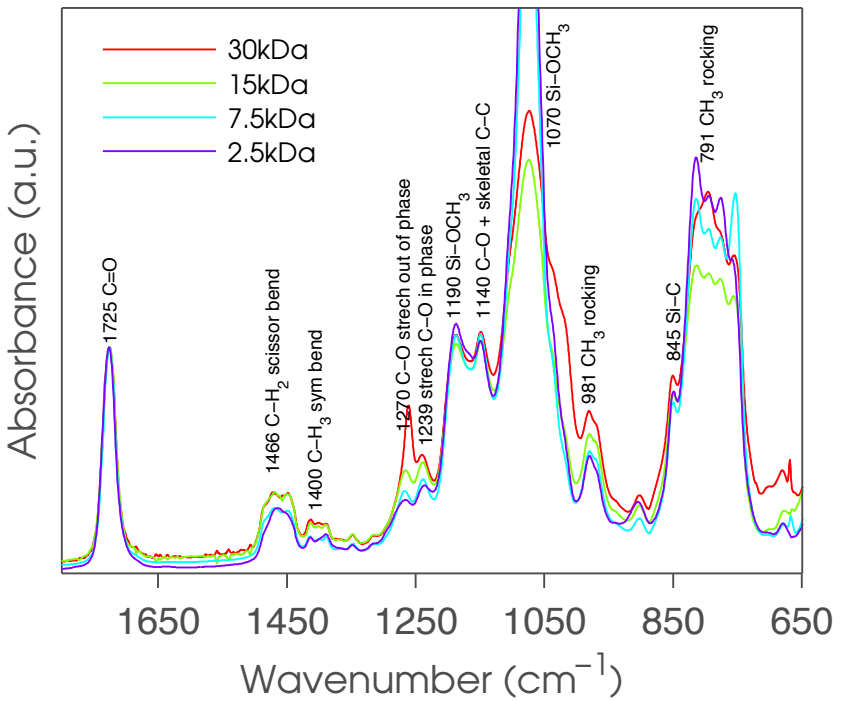


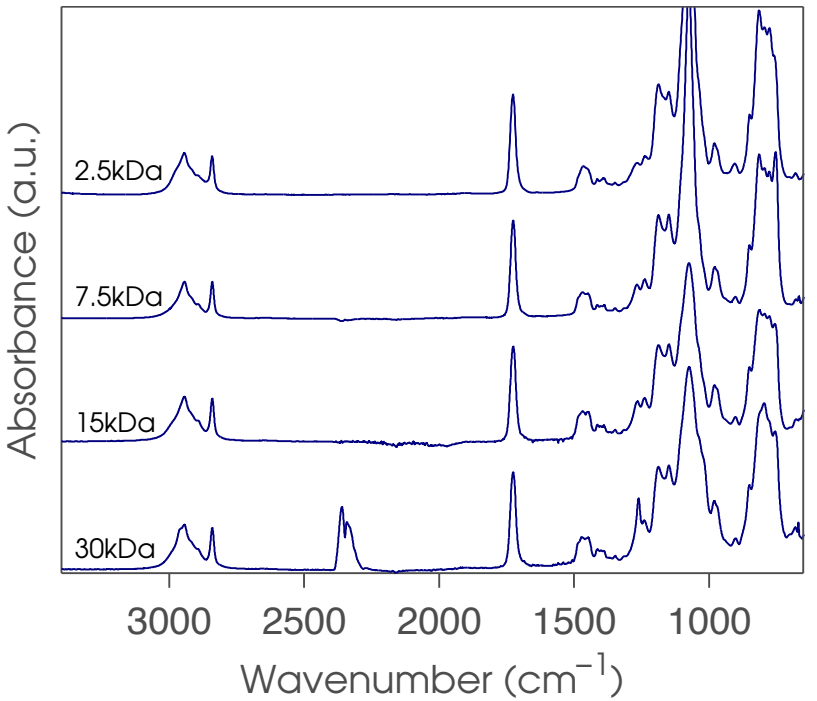
Atatic (mr) / Syndiotatic (rr)

Tageted M_w	tacticity (rr/mr)
30kDa	1.85/1
15kDa	1.80/1
7.5kDa	1.70/1
2.5KDa	1.44/1

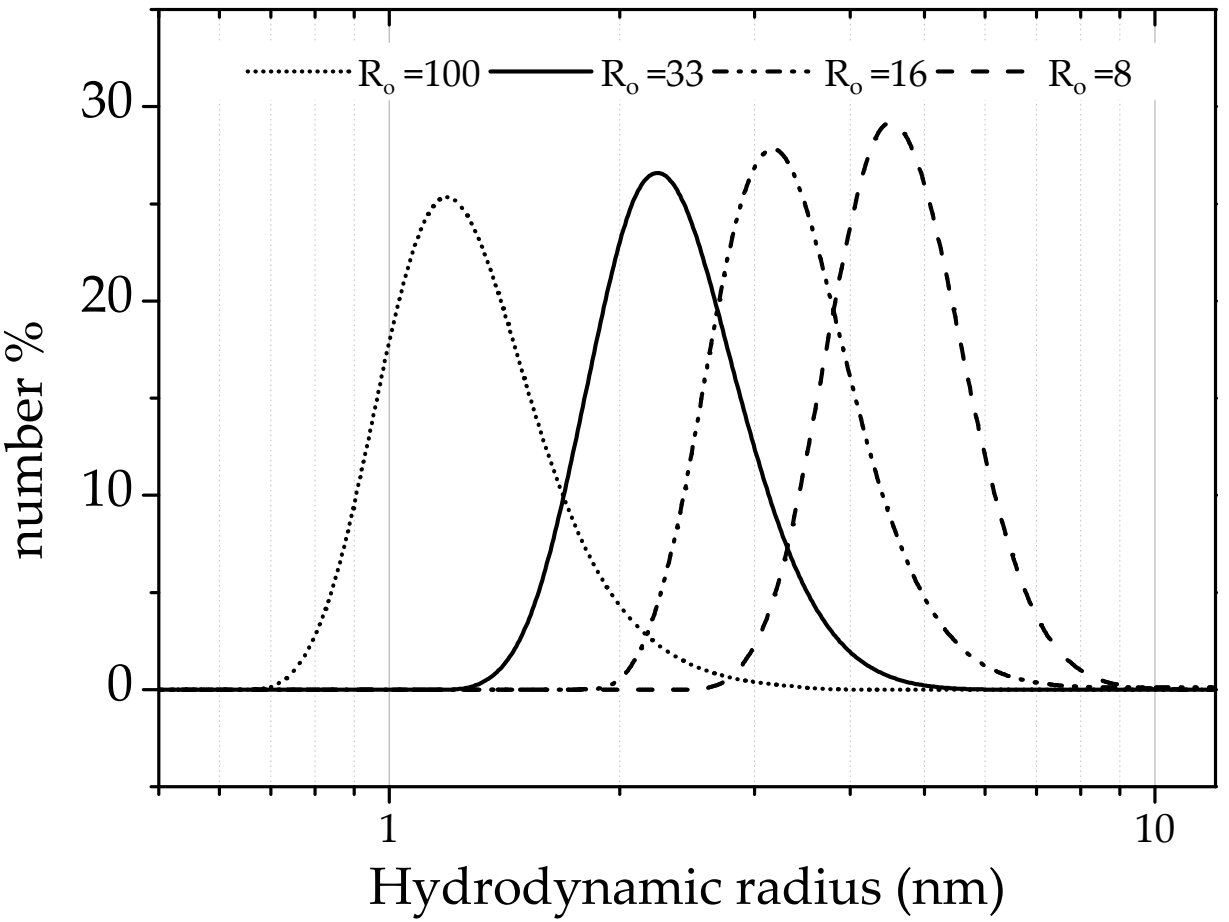
An increase of the tacticity of the polymer is observed with the increase of the molecular weight.

Chemical Structure : FTIR



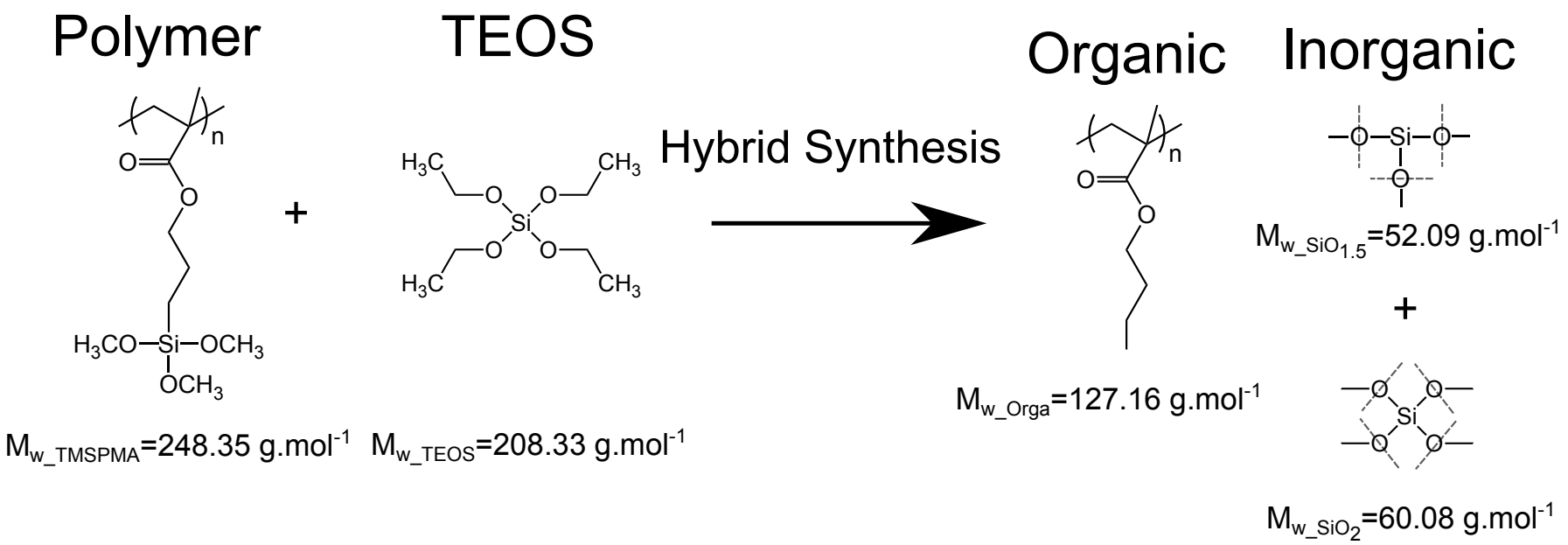


Size of the polymer : GPC & Dynamic Light Scattering



Synthesis method : Inorganic weight percent

The mass of the polymer m_{Poly} is known. The mass of TEOS, m_{TEOS}, used, is calculated to get a final Inorganic weight percent of I_w.



Inorganic Weight %

$$I_w = \frac{m_{SiO_2} + m_{SiO_{1.5}}}{m_{SiO_2} + m_{SiO_{1.5}} + m_{Organic}} \Rightarrow n_{TEOS} = \frac{\frac{I_w}{1-I_w} \cdot n_{Polymer} \cdot M_{w.Organic} - n_{Polymer} \cdot M_{w.SiO_{1.5}}}{M_{w.SiO_2}}$$

1 mol of TEOS gives 1 mol of SiO_2 and 1 mol of polymer gives 1 mol of $SiO_{1.5}$

Synthesis method : Ratio

The classical definition of the R ratio can't be used in the study. Network precursors are also introduced by the polymer which counts only 3 alkoxy groups where TEOS has 4. Therefore, H_2O and the catalyst are introduced relatively to the number of mole of alkoxy group.

Ratio definition

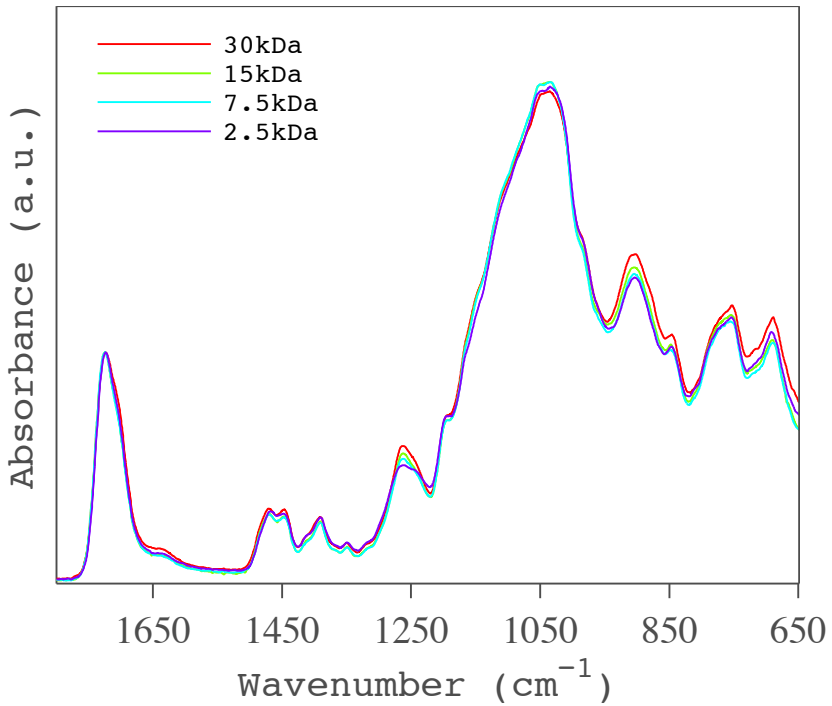
$$n_{Alkoxy} = 3.n_{Polymer} + 4.n_{TEOS}$$

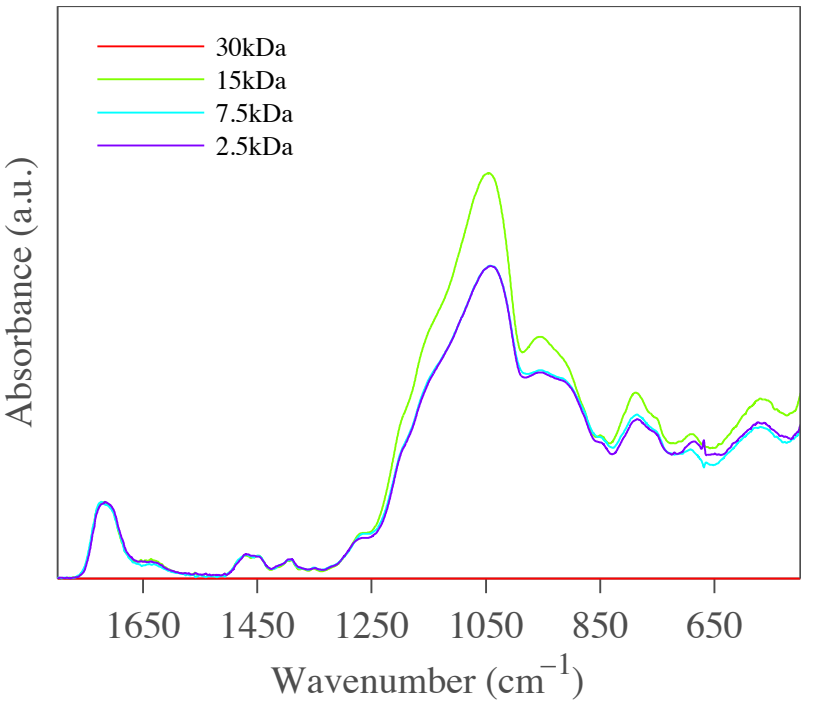
$$R_{H_2O} = \frac{n_{H_2O}}{n_{Alkoxy}} \; ; R_{Catalyst} = \frac{n_{Catalyst}}{n_{Alkoxy}} \; ; R_{EtOH} = \frac{n_{EtOH}}{n_{Alkoxy}}$$

Table : Reagent which is needed for 1g of polymer and R_{H_2O}=1, $R_{Catalyst}$=0.01, R_{EtOH}=1

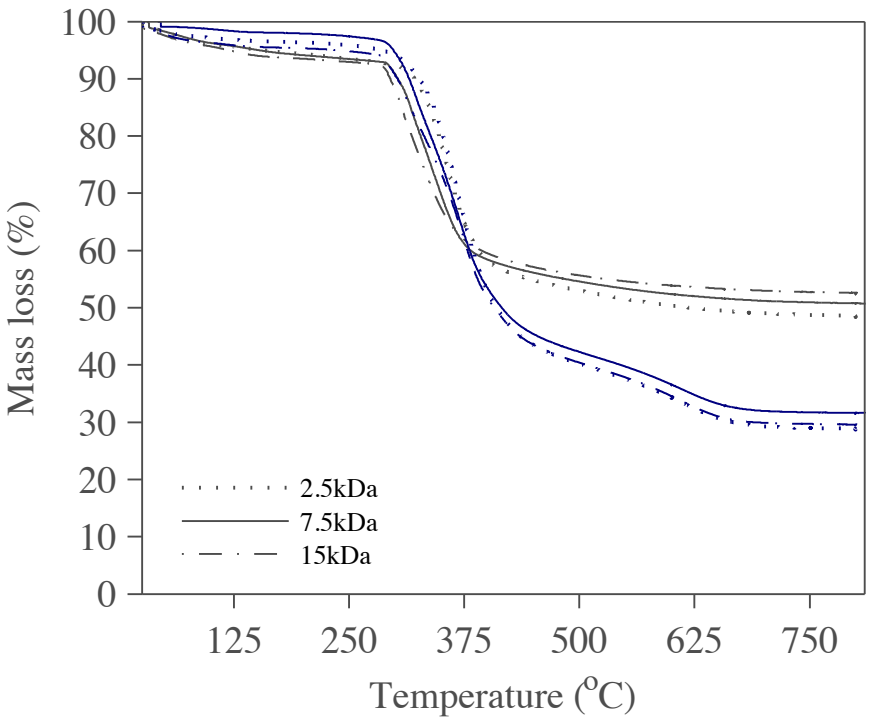
Reagent	M_w (g.mol^{-1})	D (g.mL^{-1})	n (mmol)	V (mL)
Ethanol	46.07	0.789	32.2	1.88
H_2O	18.01	1	14.3	0.258
HCL	1M	1	0.32	0.322
TEOS	208.33	0.933	5	1.123
Alkoxy group	-	-	32.2	-

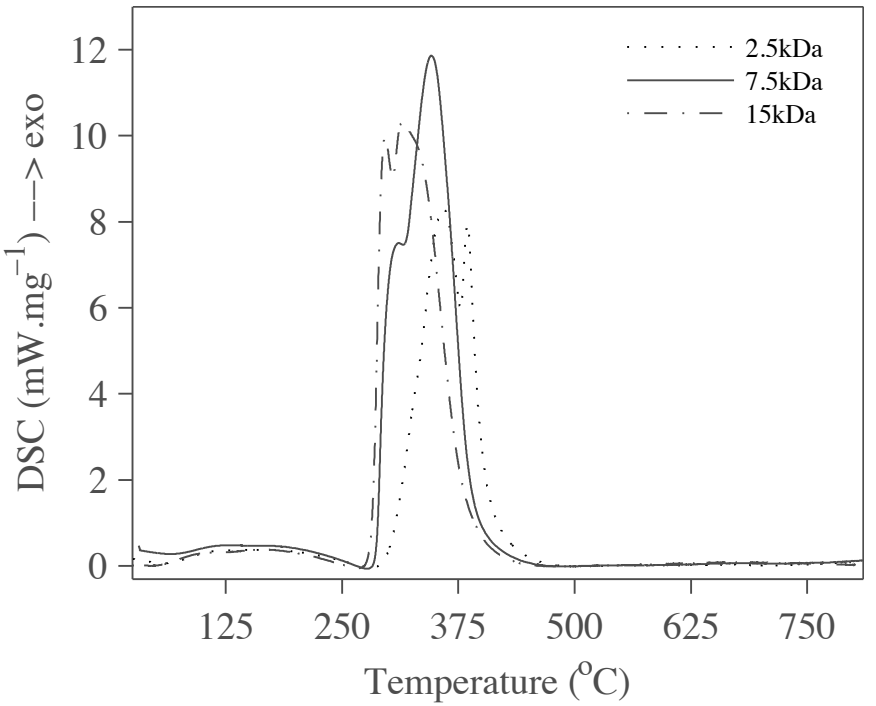
Chemical Structure : FTIR





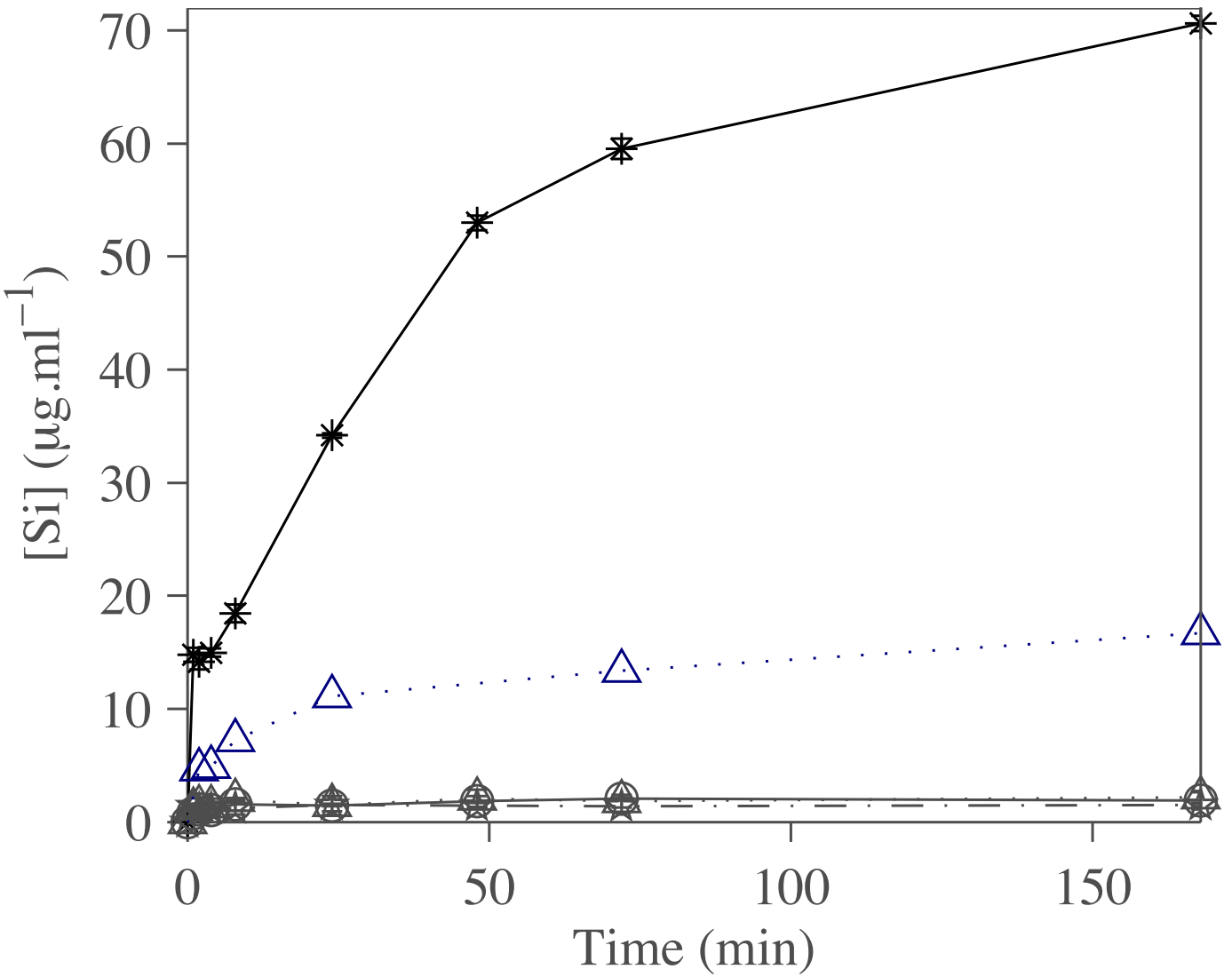
Thermoanalysis





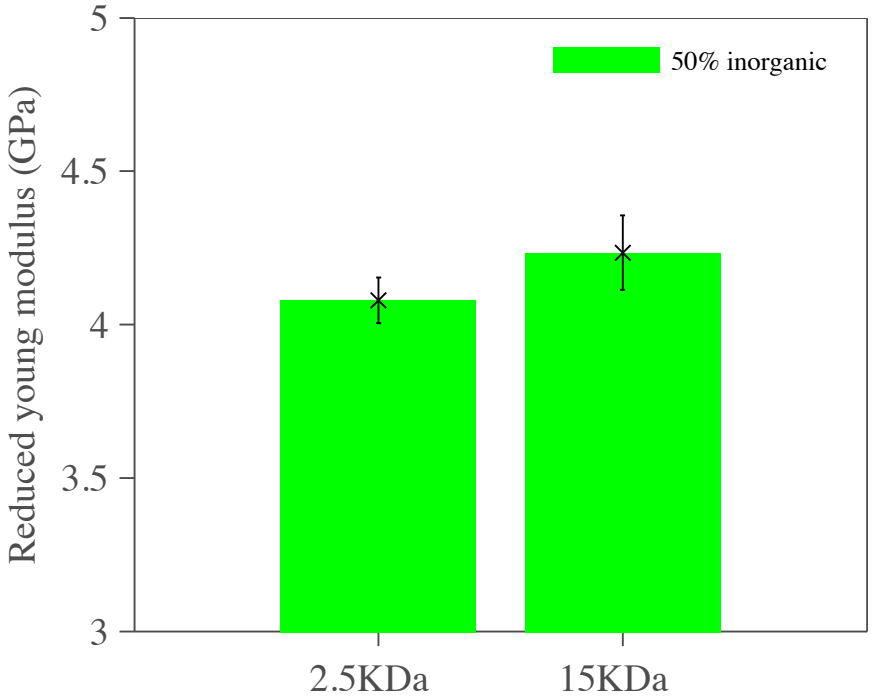
	Composition	TGA inflection pt (^{o}C)	DSC exothermic peaks(^{o}C)	Residual mass (%)
I29	2.5kDa	366.8	377.2 &394.5	28.9
	7.5kDa	368.8	313.8 & 365	31.6
	15kDa	363.2	302.7 & 368.2	29.5
I50	2.5kDa	349.3	359 & 377.5	48.5
	7.5kDa	336.4	310.9 & 336.4	50.7
	15kDa	302.1	296.2 & 315.1	52.5

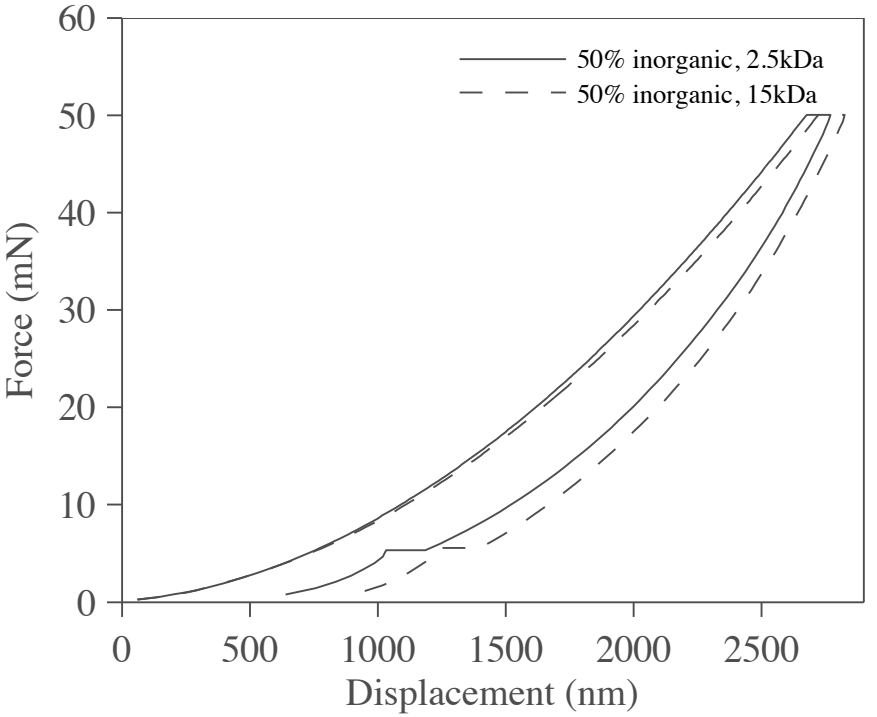
Thermoanalysis



Mechanical properties

Nonoindentation using berckvich indenter.





The end

Thanks for your attention

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Silica – polysaccharide hybrids for bone tissue regeneration

Intra-European Fellowship for career development (IEF) - Marie Curie

Yuliya Vueva

Sol-gel meeting

18th April 2013

Objectives

The aim of the project is to create new bioactive porous hybrid scaffolds that fulfil all the criteria of a scaffold for bone regeneration

Preparation and characterization of hybrids by incorporating in the sol-gel process natural polysaccharide polymers

(Carrageenans, Alginates, Celluloses)

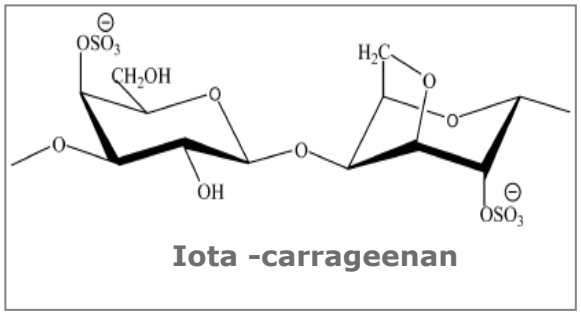
- *naturally occurring, biodegradable, nontoxic*
  - *used in the food industry and in medic, in the field of drug delivery*
    - *provide an alternative and novel method for introducing calcium into the hybrids*

The principle challenge will be to produce hybrid materials with covalent bond between the organic (polysaccharide) and inorganic (silica) part of the hybrid with controllable degradation and mechanical properties matching the host bone

Carrageenans

Interesting for hybrids application

- Iota-carrageenan produces soft and elastic gels
- *Carrageenans are anionic polyelectrolytes which gives the posibility of Ca^{2+} to be incorporated in the hybrid network*



Iota -carrageenan

Carrageenan Issues

- Solubility problems

-soluble only in water at 70°C; depending on the molecular weight; 10 mg/ml maximum

- Viscosity of solution

- difficult to obtain homogenous gels

- Modification with Si coupling agents is difficult due to the solubility issues

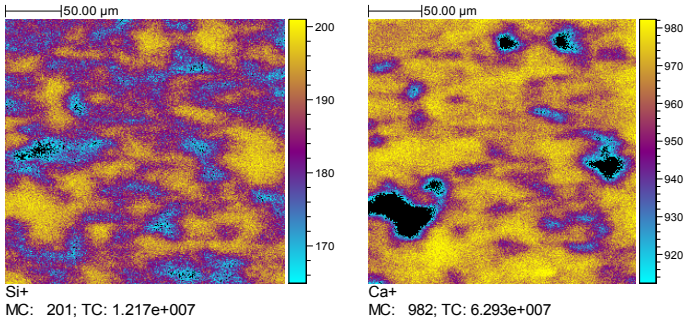
- modification with GPTMS could be performed only in heterogenous conditions

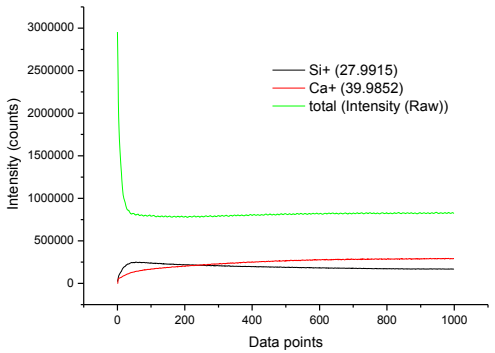
- the resultant product is insoluble

Carrageenans are sulphated linear polysaccharides of D-galactose and 3,6-anhydro-D-galactose extracted from certain red seaweeds

SIMS

40 %CAR 60 %SiO_2Ca^{2+}





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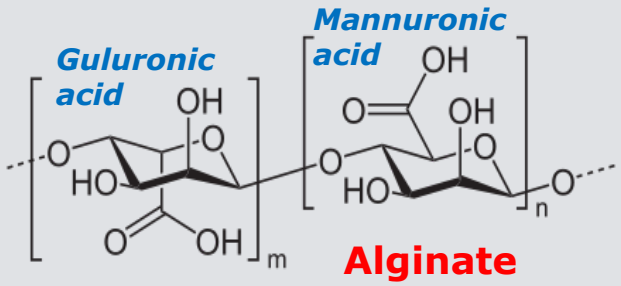
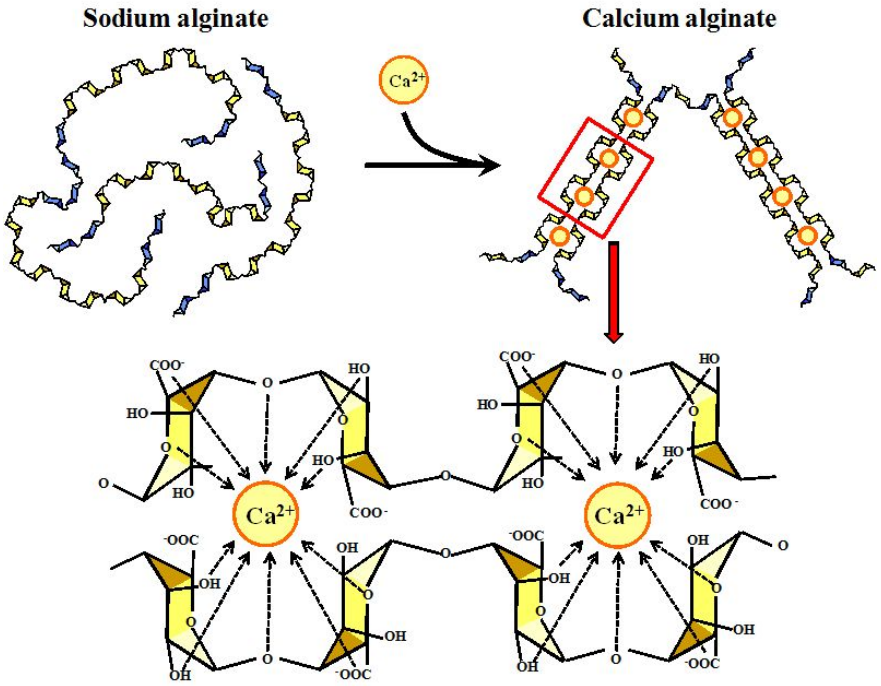
Hybrids with alginates

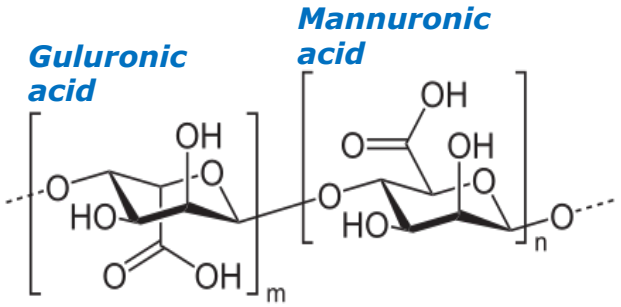


- Anionic polysaccharides derived from seaweeds
- In presence of Ca^{2+} form gels crosslinked by complexation with Ca^{2+}
- Contain carboxylic functional groups -Good potential for modification
- Potential to produce hybrids with double crosslinking (chemical and physical ionic crosslinking)



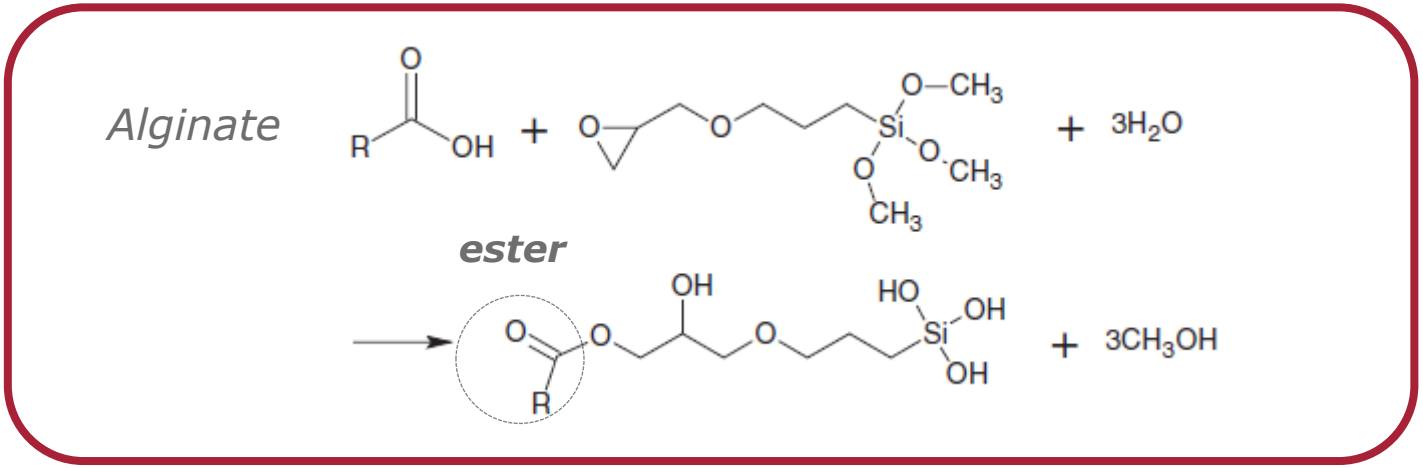
Crosslinking of alginate with Ca^{2+}

Alginate modification with GPTMS



Fictionalisation reaction

30 mg/ml Alginate in 0.01 M HCl



$RSH > RNH_2 > R_2NH > RCOOH > SiOH >> ROH > H_2O$

Relative reaction rates of different functional groups toward epoxy groups

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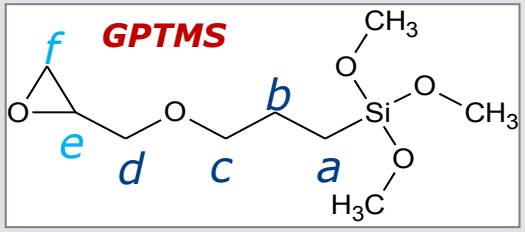
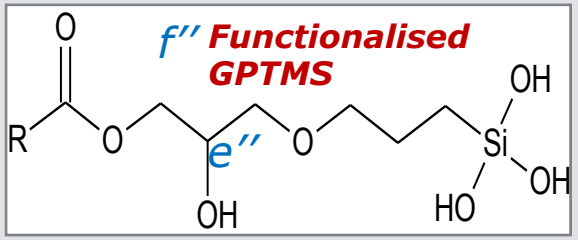
^{1}H NMR





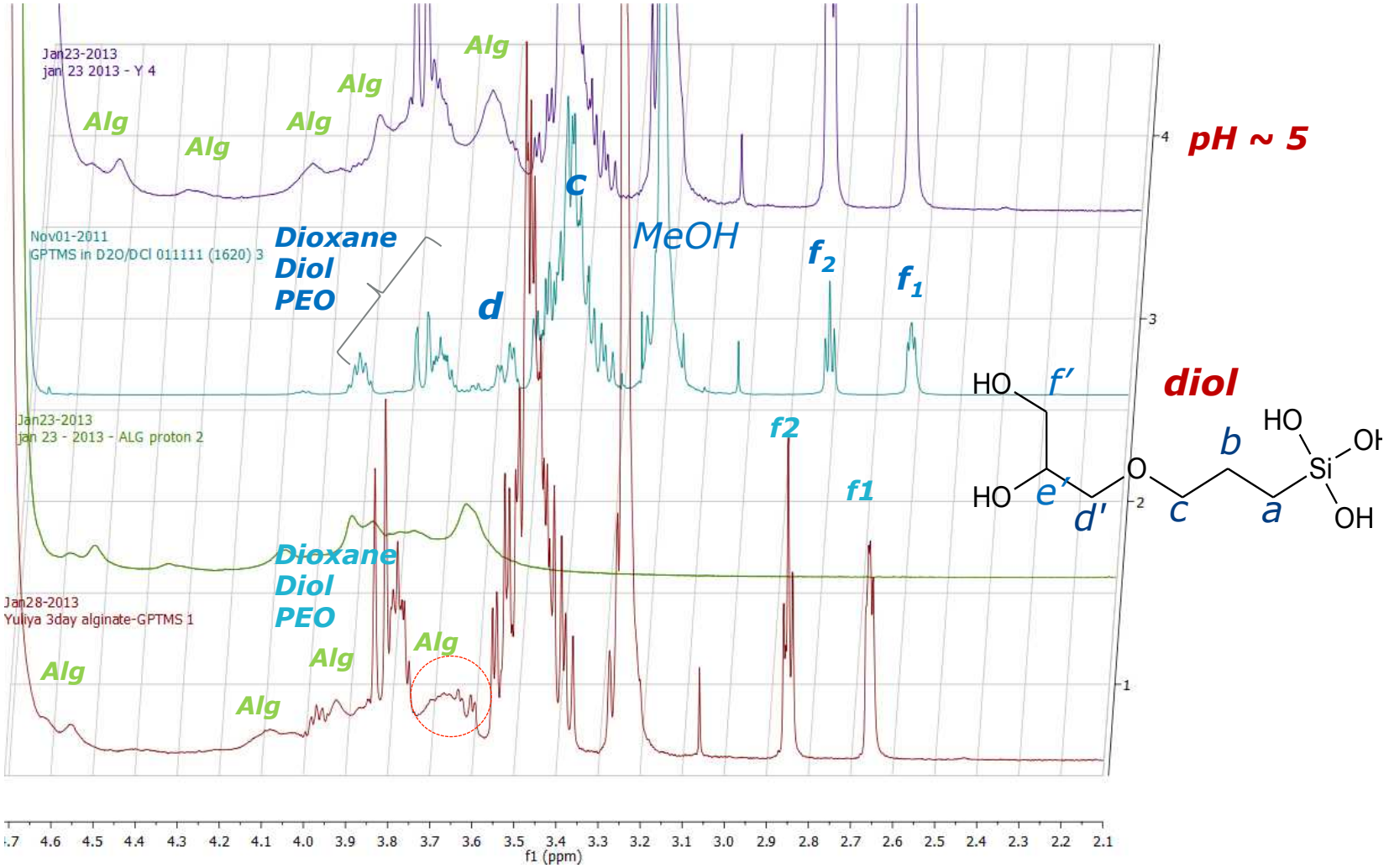
GPTMS + Alg 12h

GPTMS in D_2O/DCl

Courtesy of Louise

Alginate

GPTMS + Alg 3 days



pH ~ 5

diol

Epoxide opening versus silica condensation during sol-gel hybrid biomaterial synthesis, Luca Gabrielli, Laura Russo, Ana Poveda, Julian R. Jones, et. ***DOI: 10.1002/chem.200***

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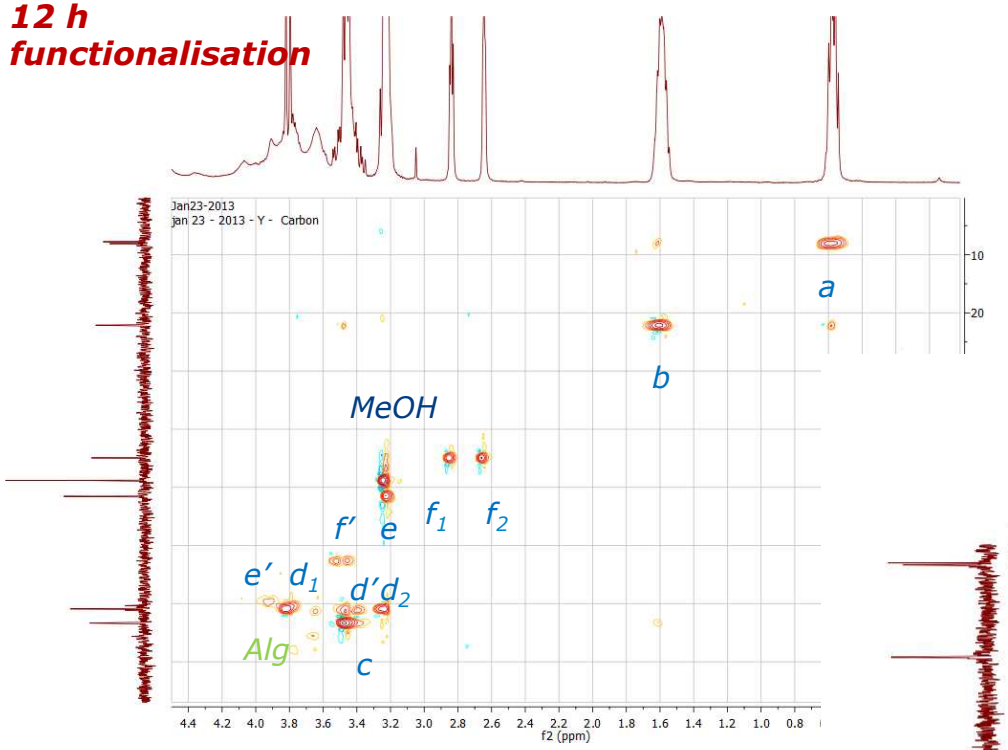
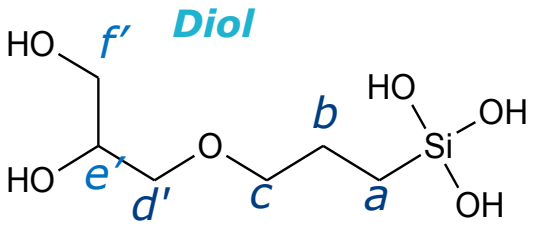
HSQC of functionalised with GPTMS Alginate

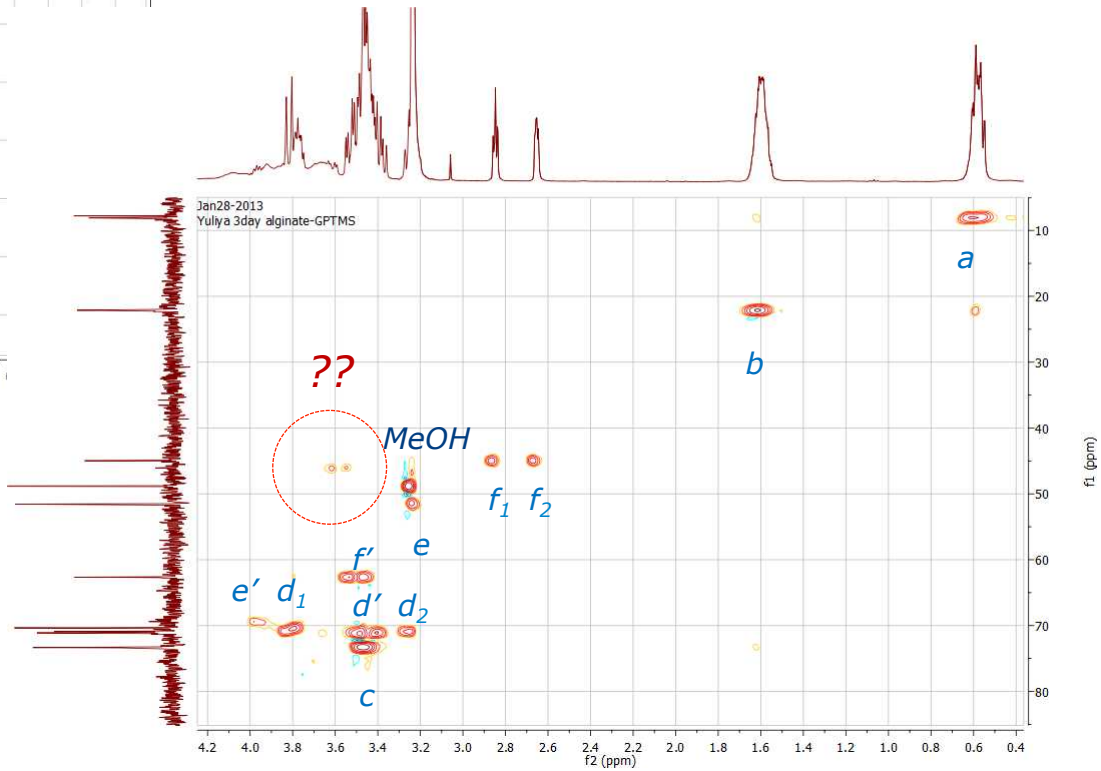
12 h functionalisation



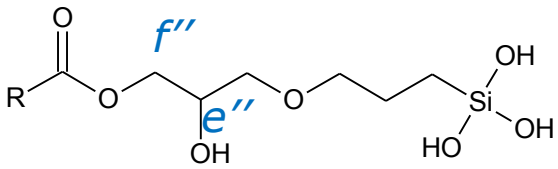
Diol



3 days functionalisation



Functionalised GPTMS



Issues and conclusions

• Polymer concentration is not high enough to achieve suitable ^{1}H and ^{13}C NMR signals

• This is not clear if the covalent linkages are lost in the background along with the polymer signal or is no covalent coupling occurring

• The epoxy ring is not fully opened during fictionalisation of alginate at pH 5. The main compounds detected are diol, dioxane and PEO.

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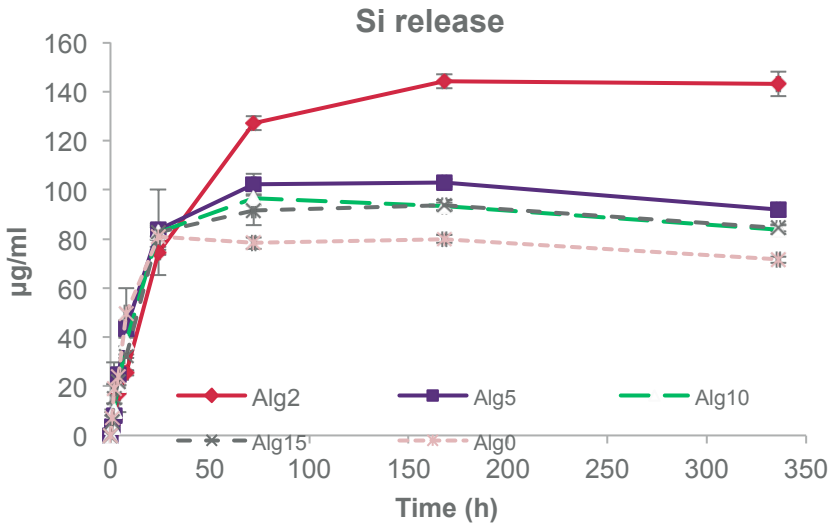
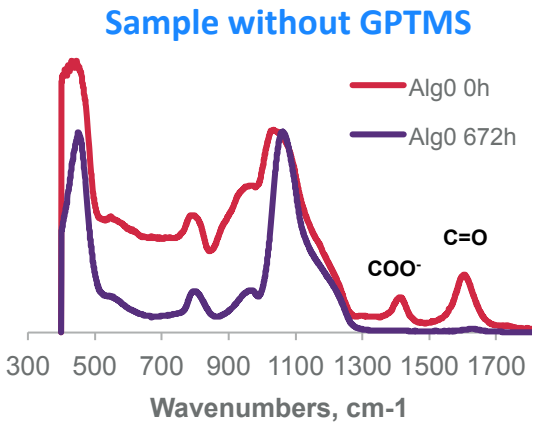
IEF Marie Curie – HABER

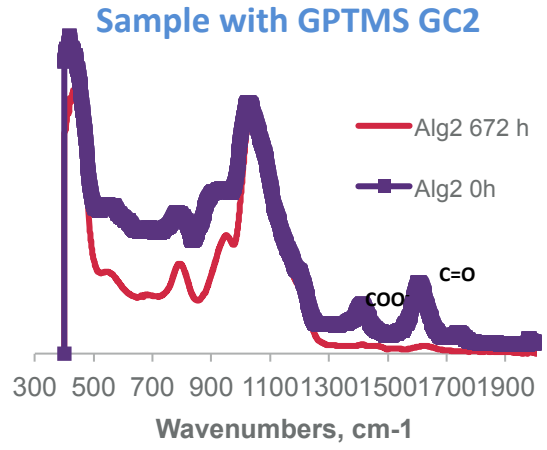
Dissolution study of alginate-silica hybrids

Dissolution study in Tris



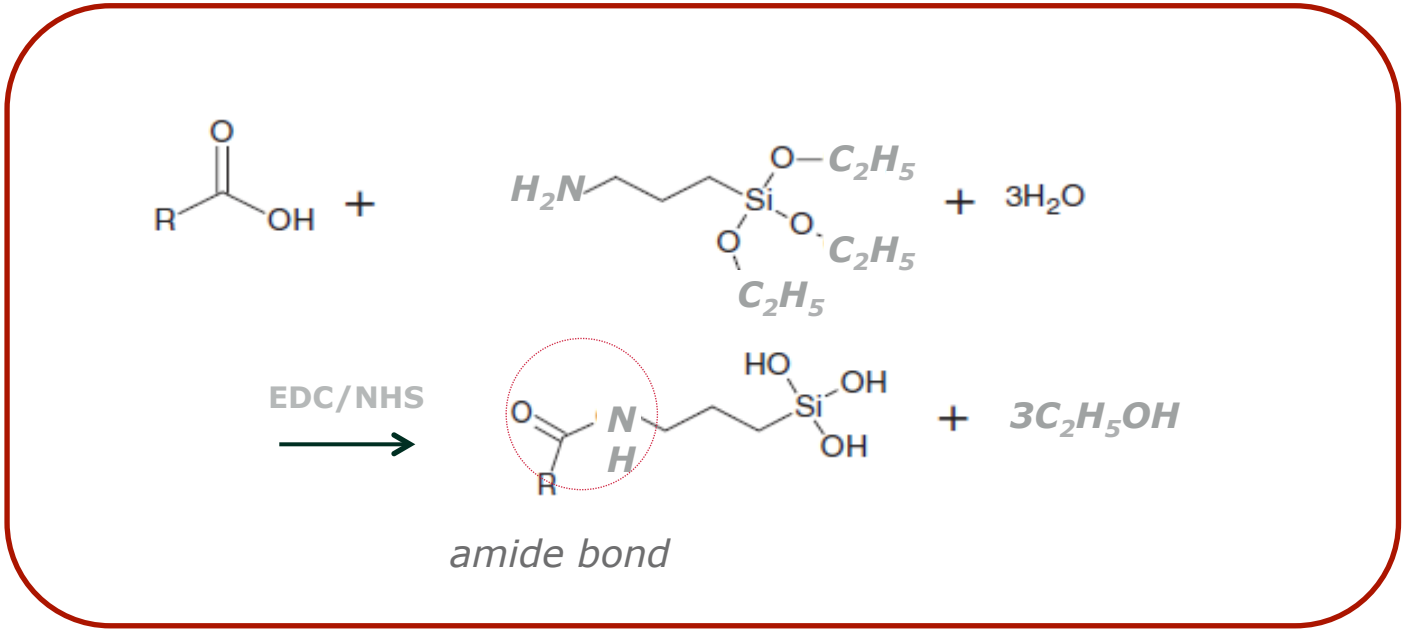


- *Early release of silica is rapid when alginate is not coupled with GPTMS.*
- *No alginate after 4 weeks in TRIS for the sample without GPTMS*
- *The samples coupled with GPTMS showed very weak bands corresponding to carboxylic groups of alginate*
- *Most of the polymer had dissolved after 4 weeks in Tris*

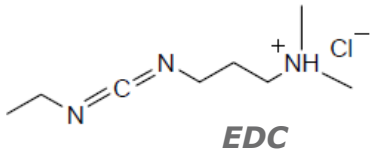


Modification of Alginate with APTES

Reaction utilizing carbodiimide chemistry

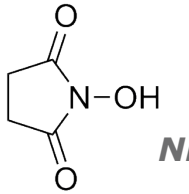


amide bond



EDC

1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride



NHS

N-Hydroxysuccinimide

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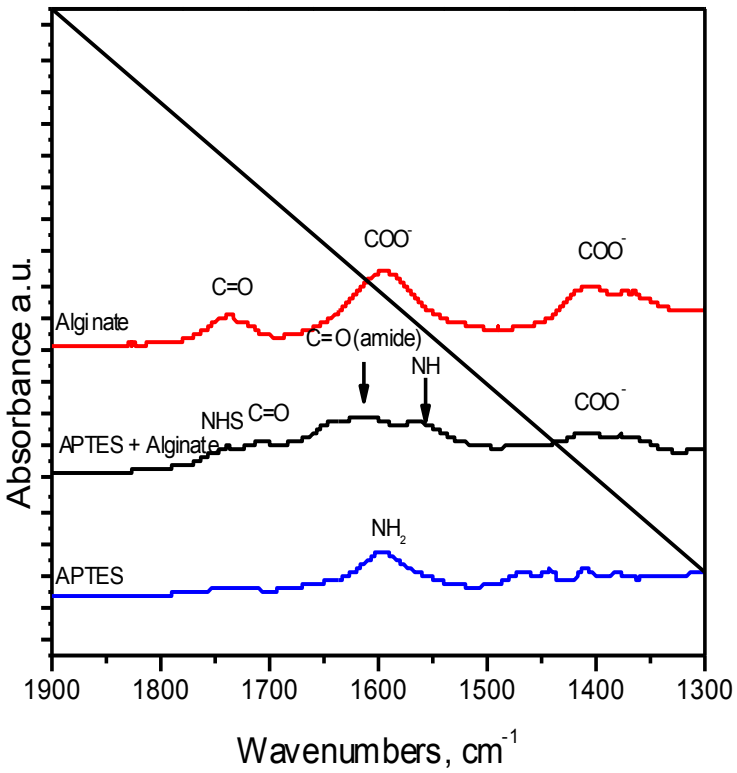
ATR-FTIR of alginate modified with APTES

Preliminary study of the reaction of APTES with Alginate



pH = 6

Formation of amide bond

After dialysis of Alginate-APTES solutions the APTES is still present in the solution. – Functionalised Alginate

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Further work

- *Optimization of reaction conditions for modification of Alginate with APTES*
- *Evaluation of substitution degree by ICP and NMR*
- *Optimization Alginate-silica hybrid synthesis*