A New Approach to Produce Starch Graft Copolymers and Grafted Starch Nanoparticles via Nitroxide-Mediated Polymerization

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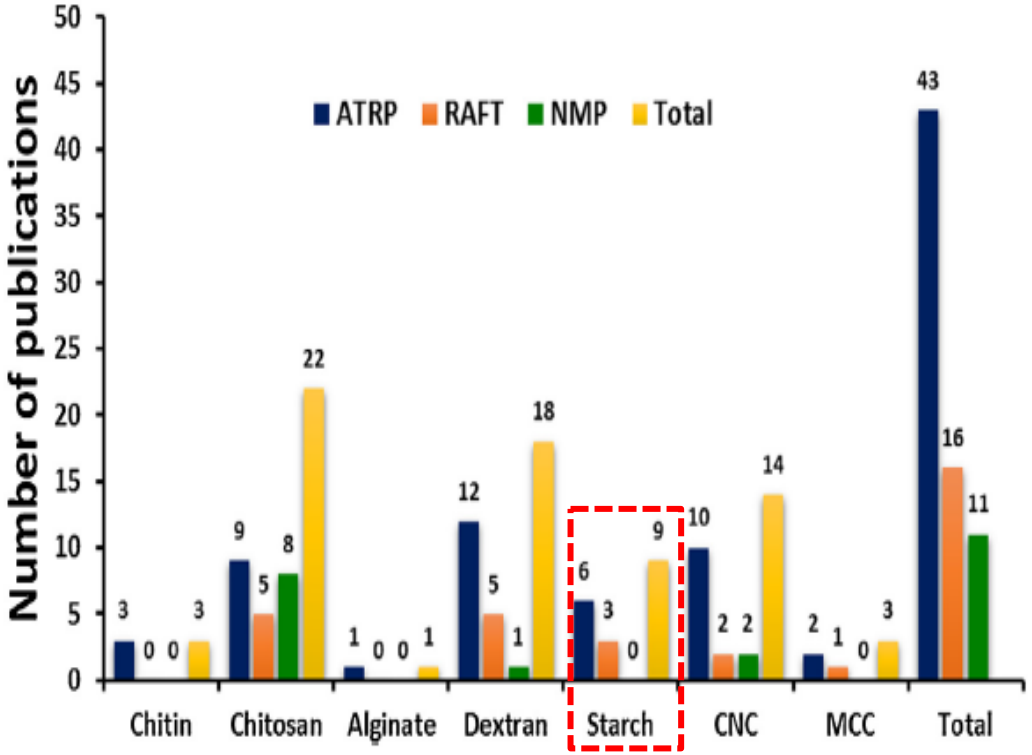
International Symposium on Bioplastics, Biocomposites and Biorefining || July 24 - 27, 2018 || Guelph, ON, Canada

Motivation

Development of new products:

- using renewable materials
- low viscosity
- paper coatings





Number of publications of **RDRP** of polysaccharides as of 2017.[1]

[1] **O. Garcia-Valdez et al., *Prog. Polym. Sci.* 2017, 76, 151-173.**

Motivation

Objective:

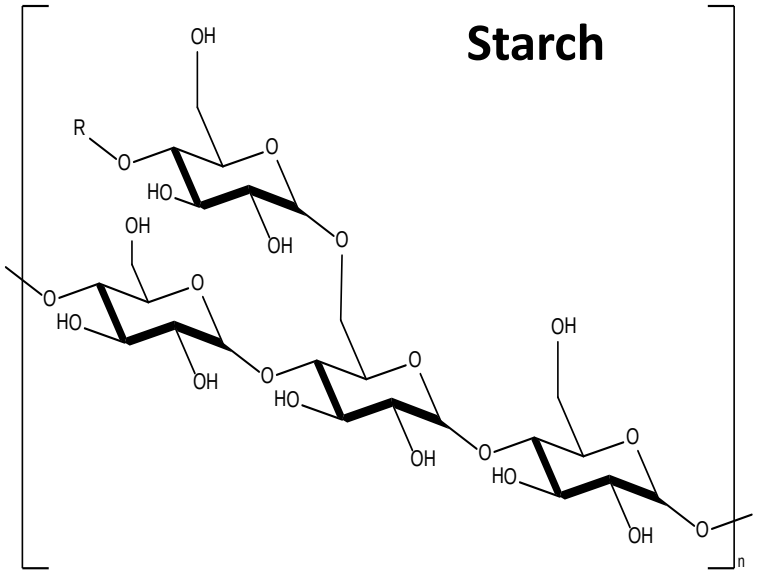
- Design modified starch graft copolymers and starch nanoparticles that are compatible with synthetic polymers

Potential Applications:

- Paper coatings
- Bio-filler, packaging, agriculture

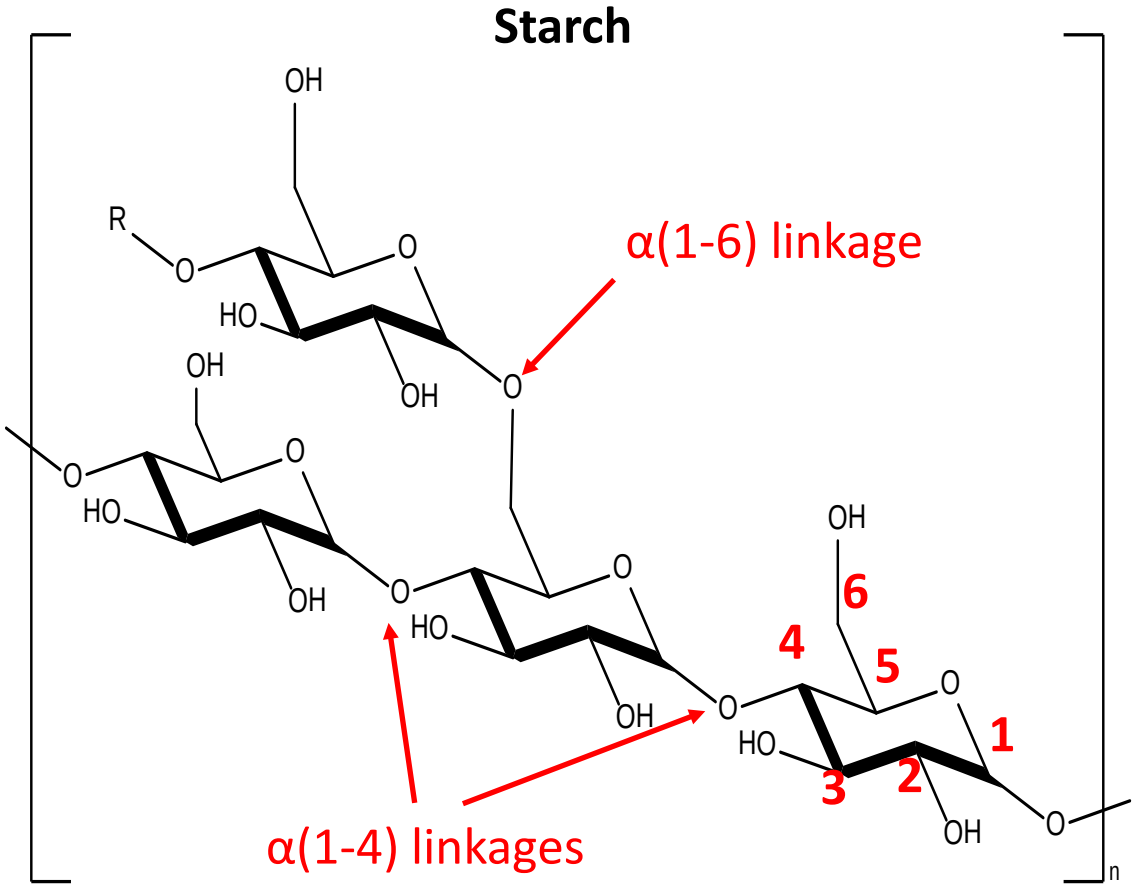
Challenge:

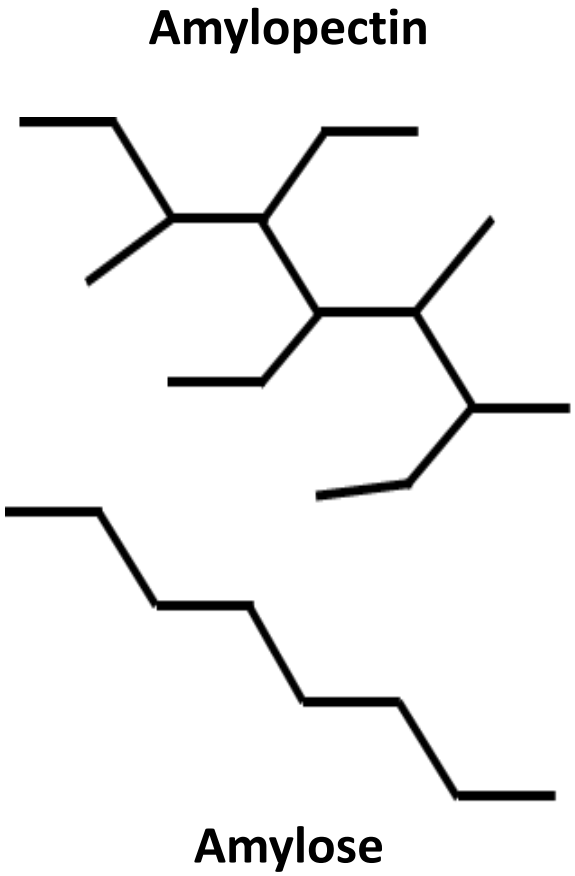
- Bio-polymer compatibility in synthetic latexes/matrices



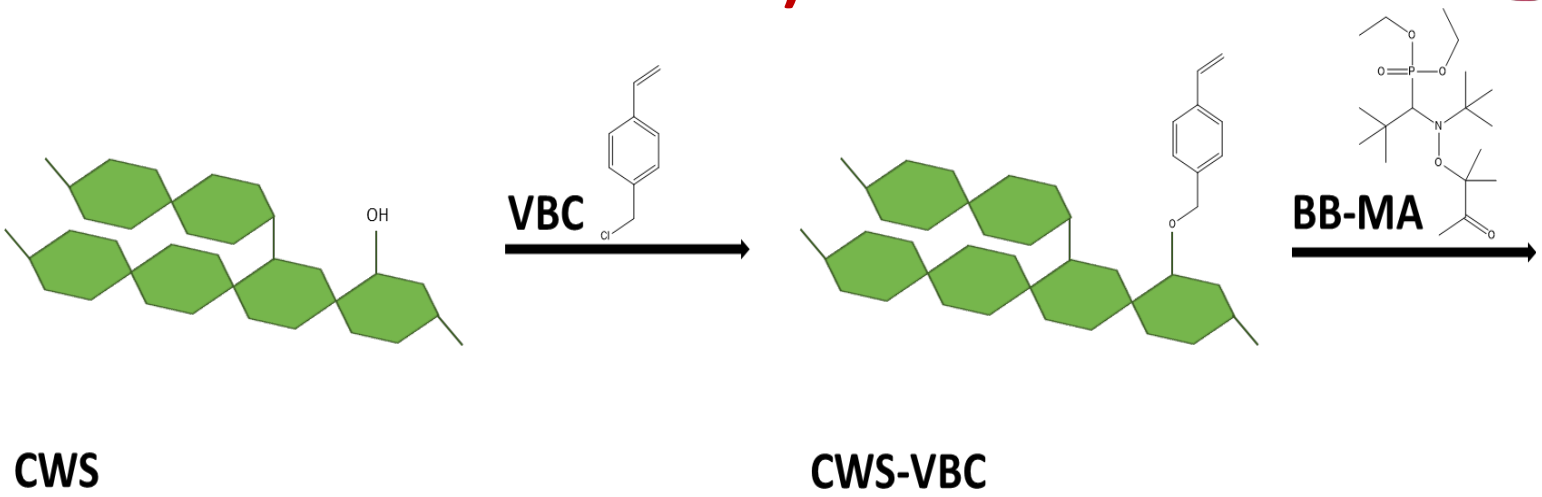


Starch Structure



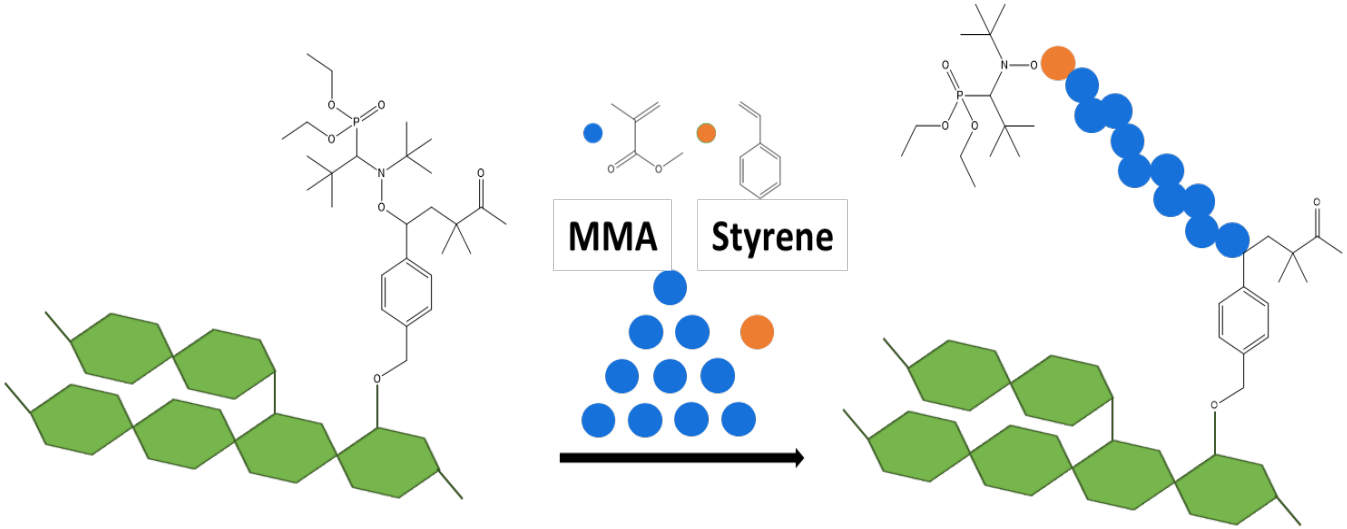


General Approach: Modification of CWS (Cold water soluble starch)



CWS

CWS-VBC



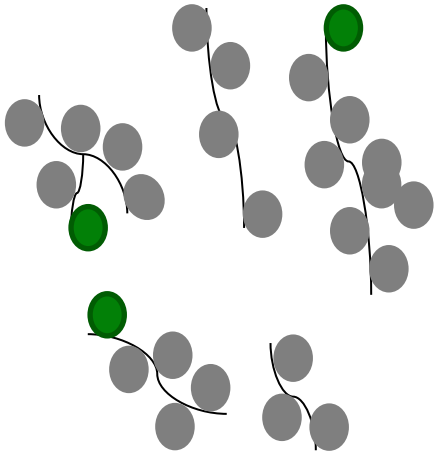
CWS-macroinitiator

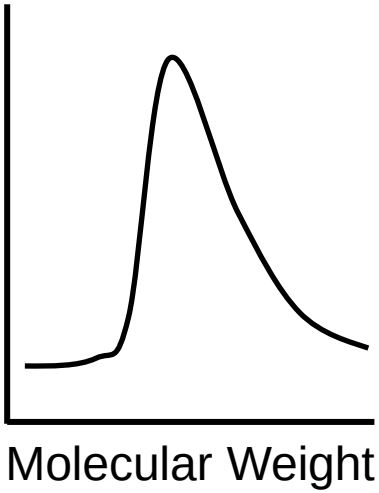
CWS-*g*-(MMA-*co*-ST)

Reversible Deactivation Radical Polymerization (RDRP)

Free Radical Polymerization:

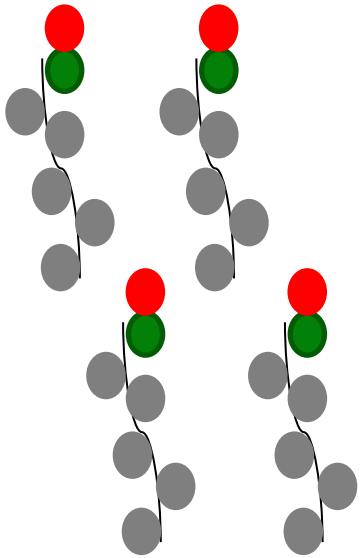
- Short growth time
- Continuous initiation
- Inexpensive and widely used

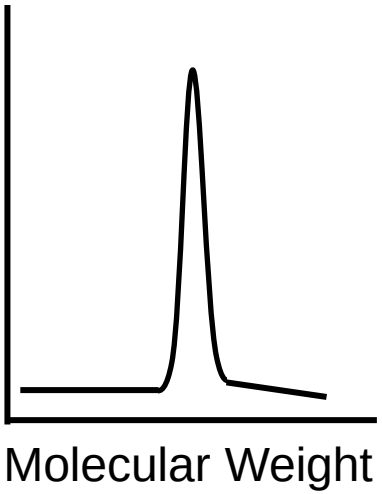




RDRP:

- Long growth time
- Instantaneous initiation
- Control over MW and narrow dispersity

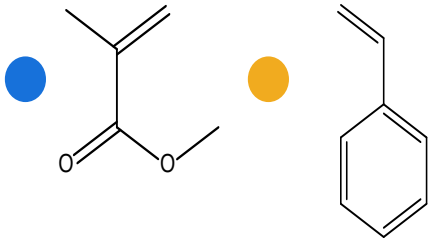




RDRP: Nitroxide-Mediated Polymerization

Why use RDRP?

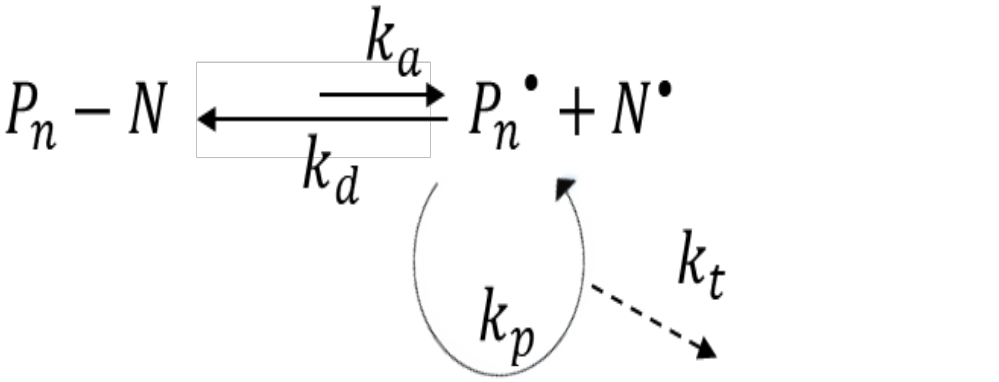
- Need fine control over starch content (>90%)
- NMP offers simple unimolecular mechanism



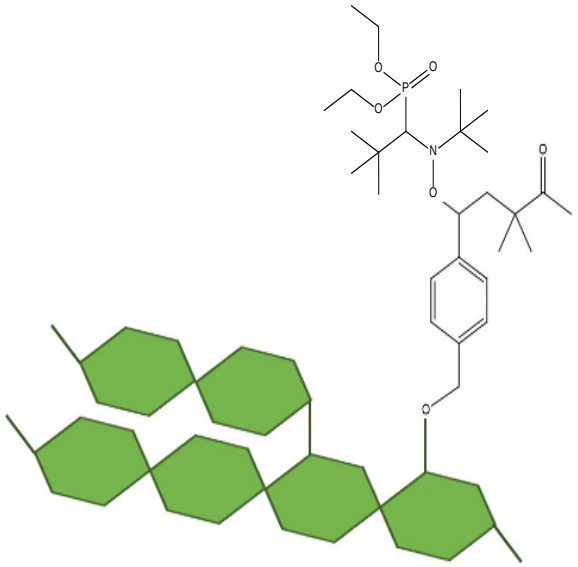
MMA Styrene

- Introduce reversible competing reaction
- Homolysis of alkoxyamine at elevated temperature



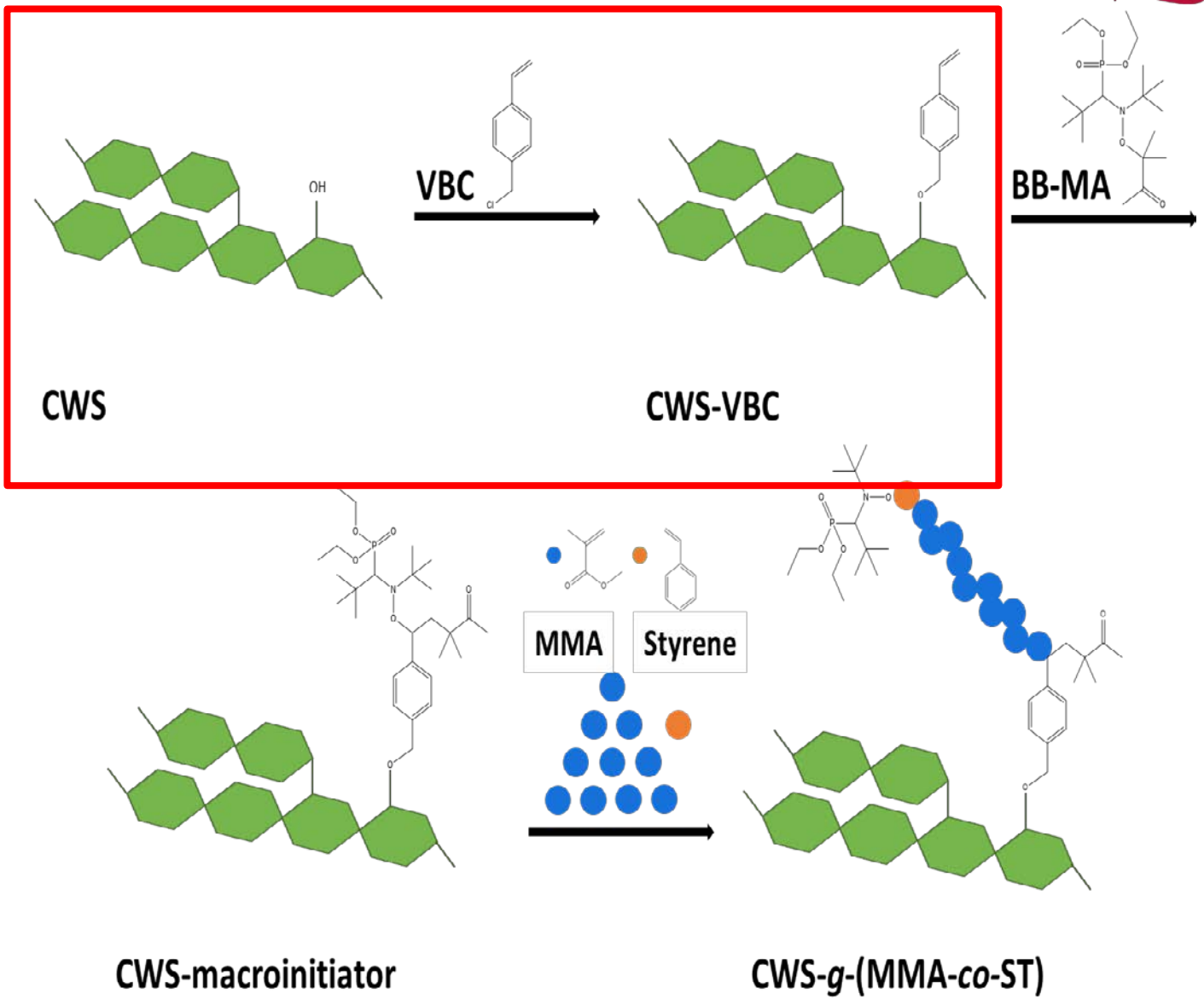


Propagation Termination



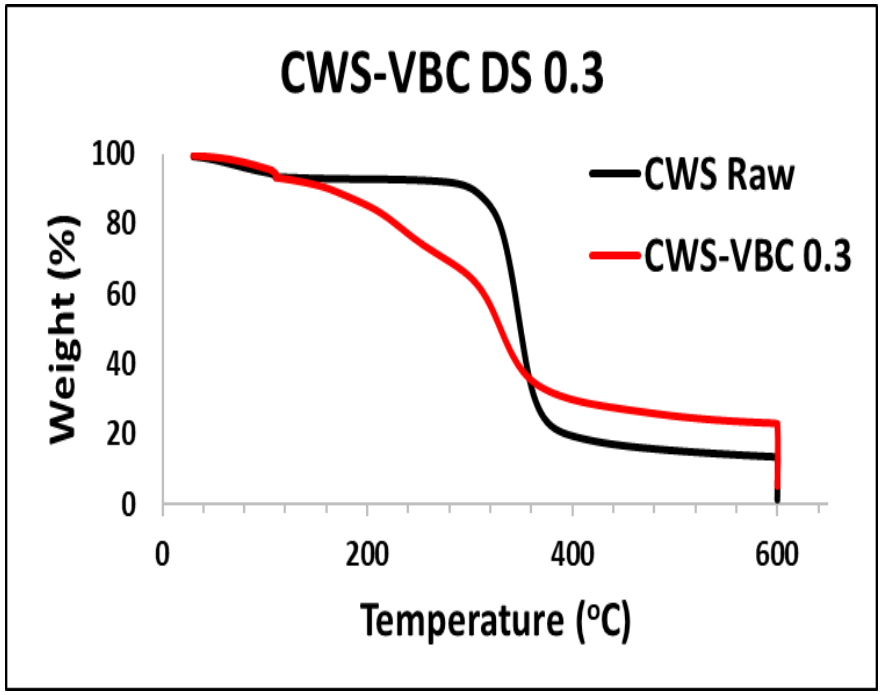
CWS-macroinitiator

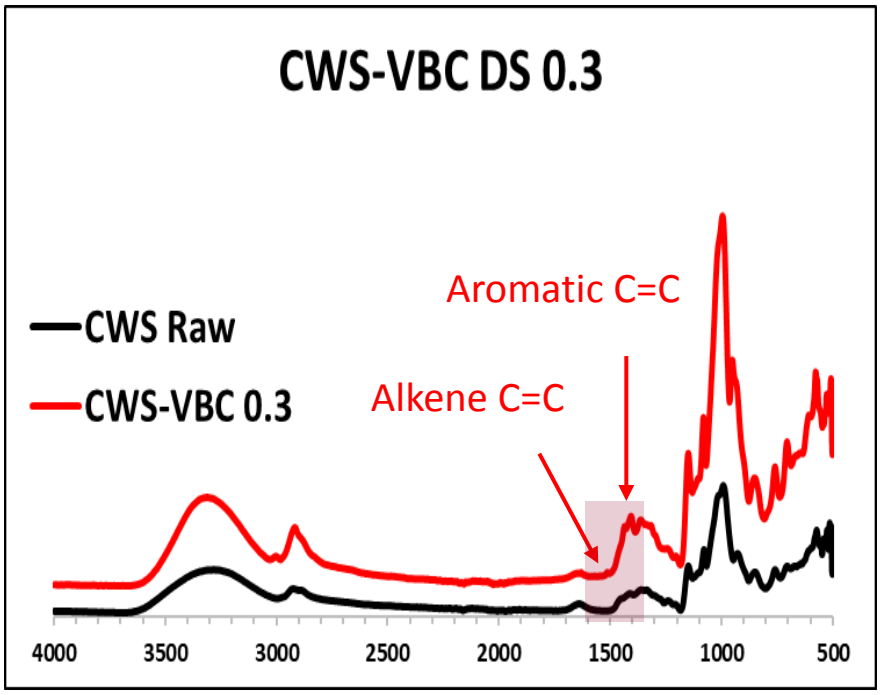
Modification of CWS with VBC



Modification of CWS with VBC

- Shift in TGA profiles
- VBC peaks observed in FTIR

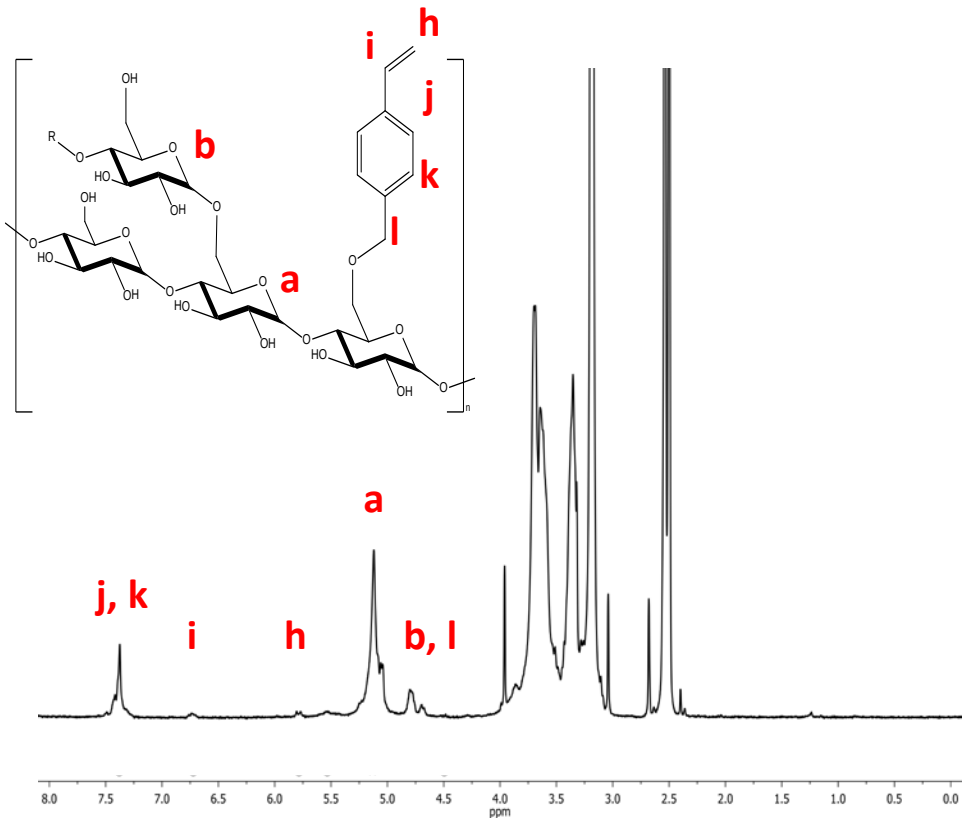




Modification of CWS with VBC

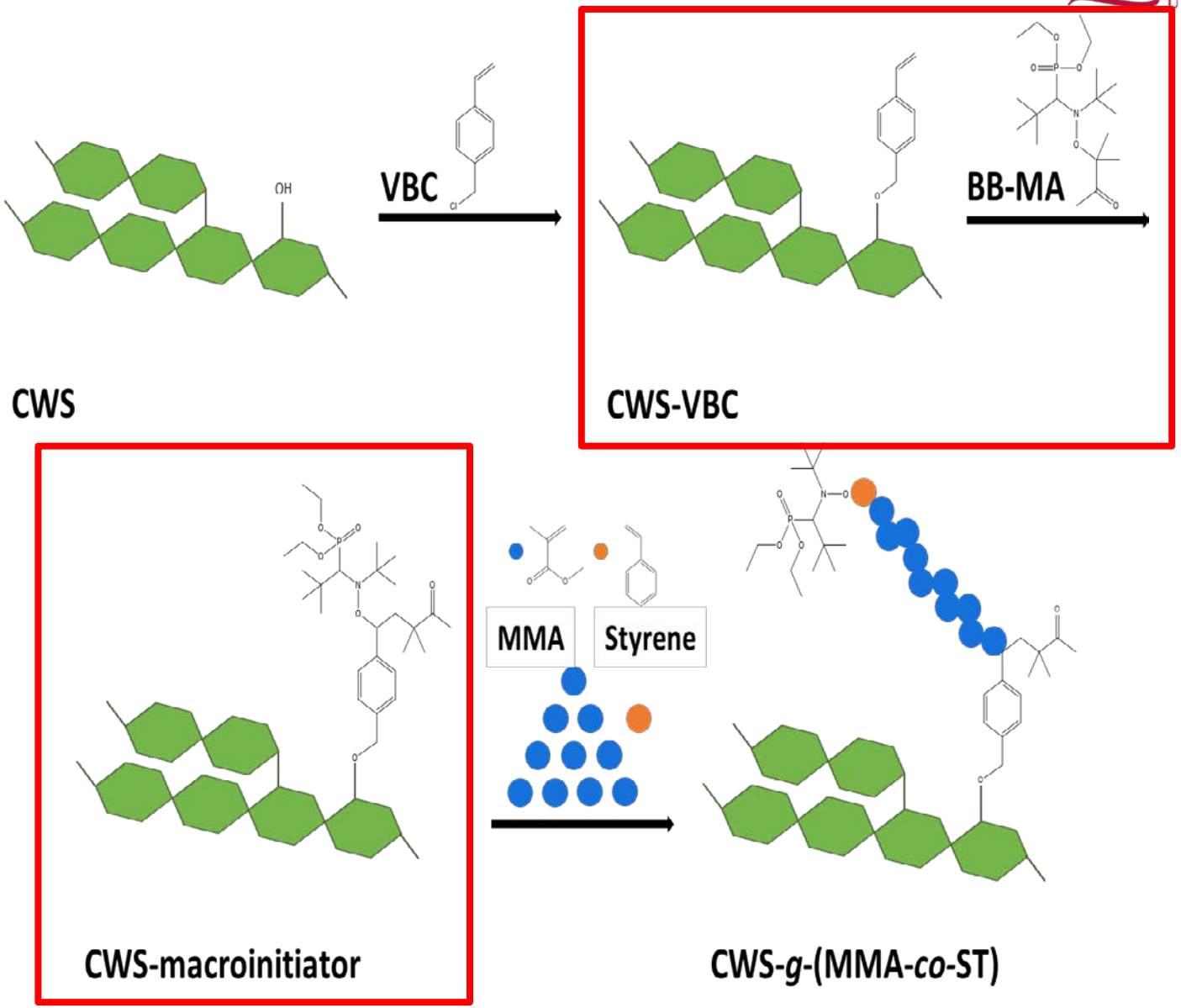
Theoretical DS	Experimental DS 60°C
0.3	0.059 +/- 0.005

DS=degree of substitution



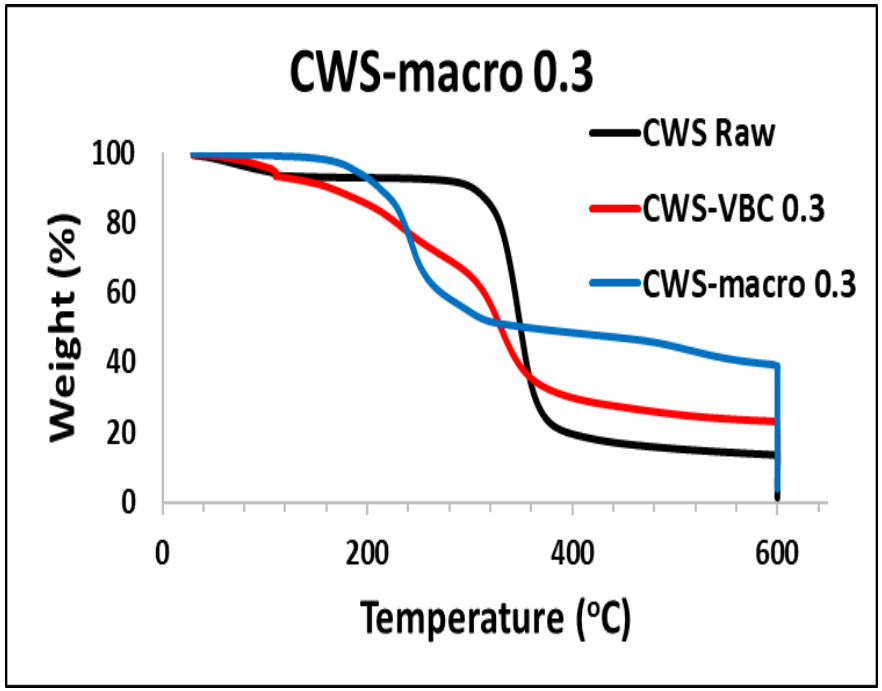
CWS-VBC 0.3 in DMSO-d_6 – 60°C – 0.25uL TFA

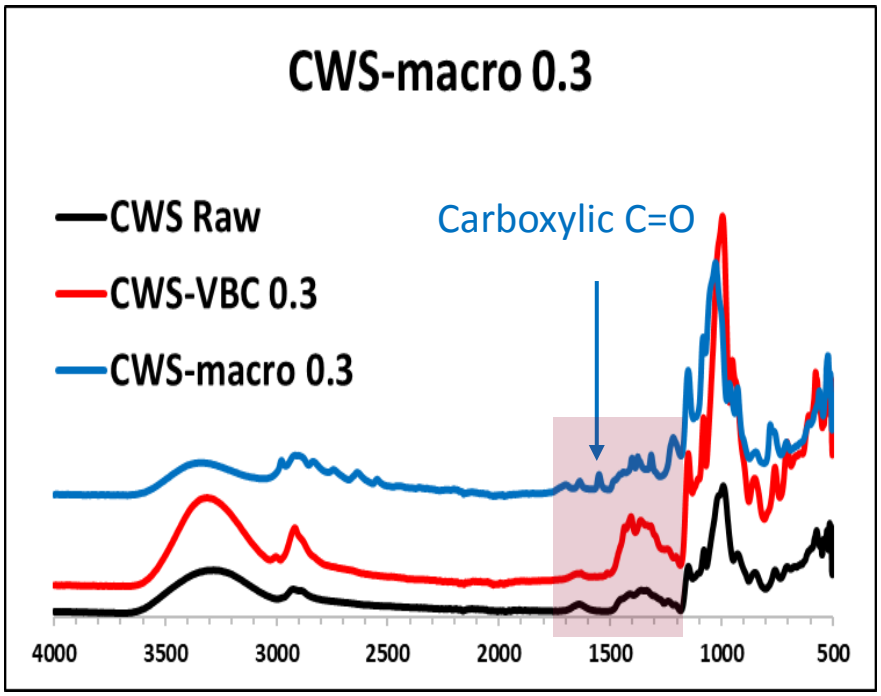
Synthesis of CWS-macroinitiator



Synthesis of CWS-macroinitiator

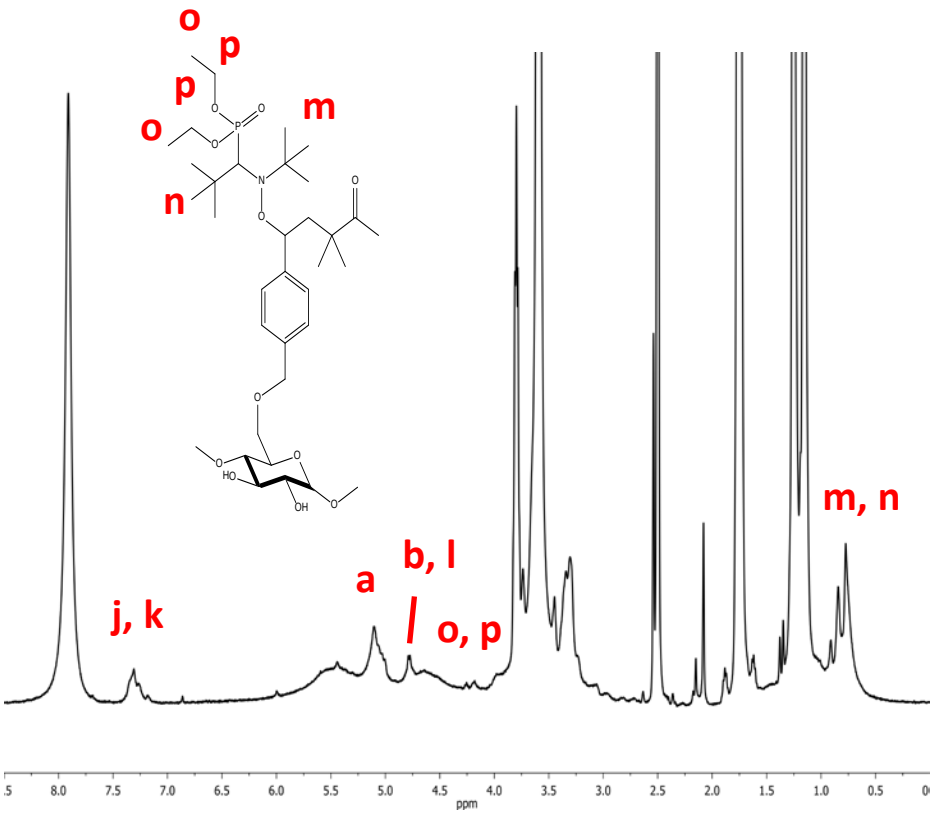
- Shift in TGA profiles
- BlocBuilder® (BB-MA) peaks observed in FTIR





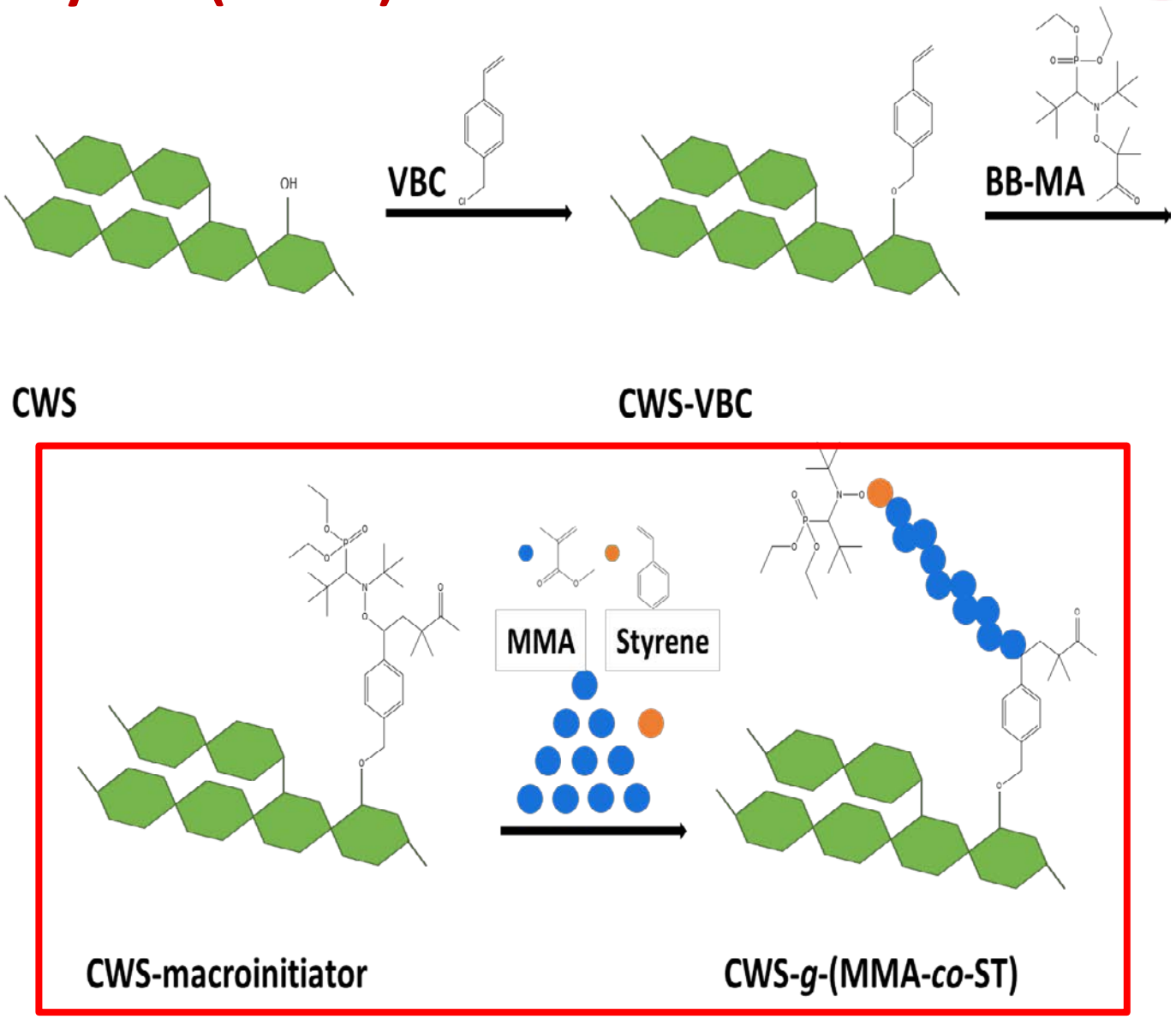
Synthesis of CWS-macroinitiator

Elemental Analysis	CWS-VBC Weight (%)	CWS-BB Weight (%)
C	46.87 +/- 0.01	46.56 +/- 0.28
H	6.50 +/- 0.02	6.78 +/- 0.06
N	**0**	**0.13 +/- 0.03**



CWS-macro 0.3 in DMSO-d_6 – Room Temperature

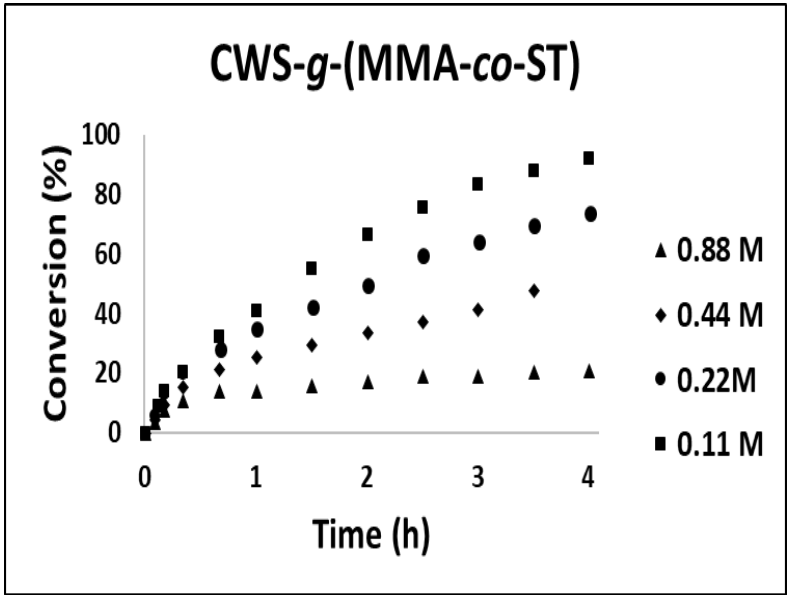
Grafting From Polymerization with Methyl Methacrylate (MMA)

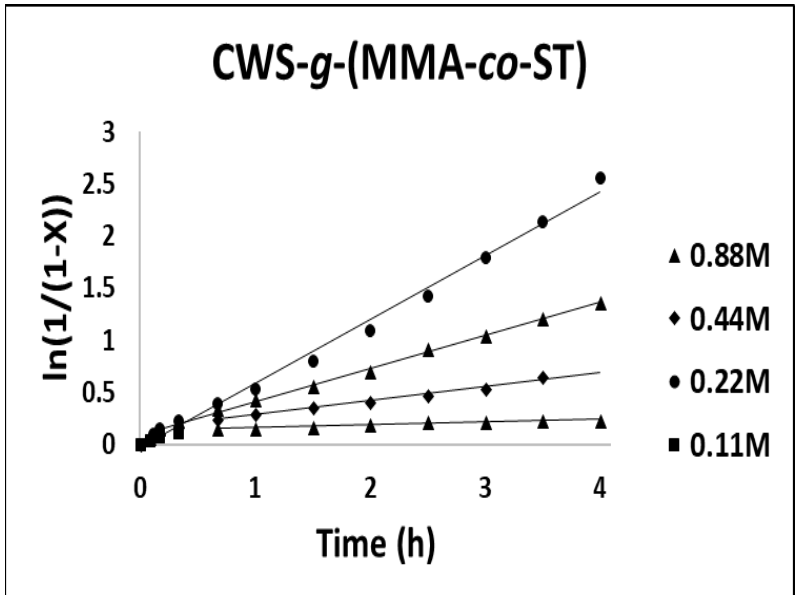


CWS-*g*-(MMA-*co*-ST)

- Varied monomer concentration [M] (monomer:starch ratio)
- Constant MMA:ST ratio (9:1)

[M]	Time to make 60% starch hybrid	Graft polymer dispersity
0.88M	6 min	1.46
0.44M	10 min	1.42
0.22M	25 min	1.44
0.11M	90 min	1.33



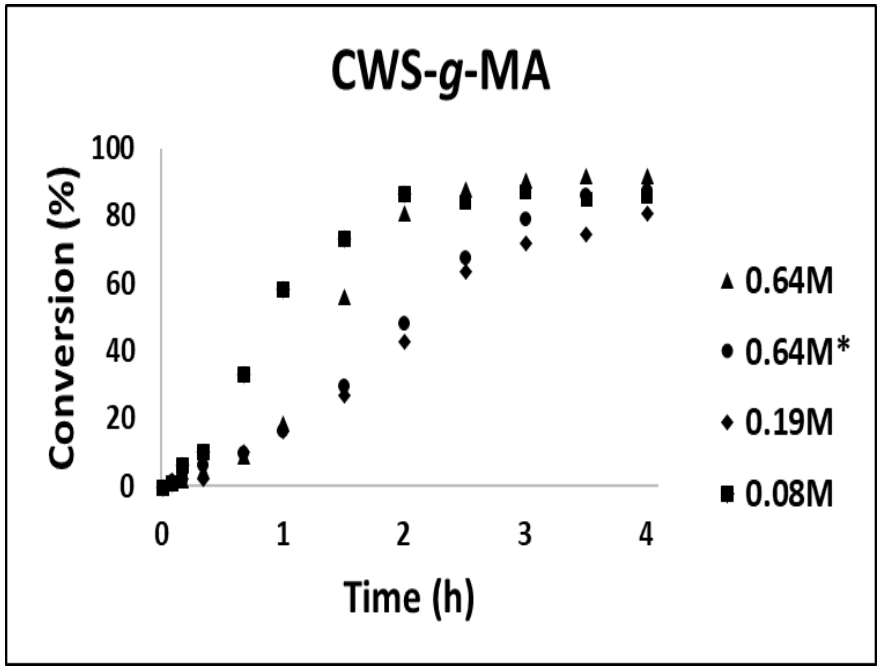


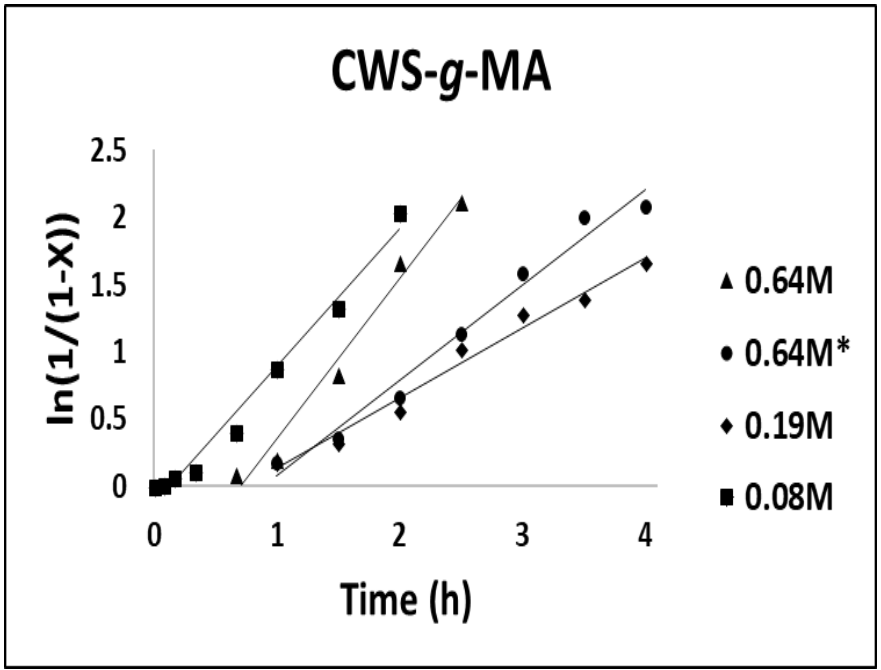
CWS-*g*-MA (Methyl Acrylate)

- Varied monomer concentration [M] (monomer:starch ratio)

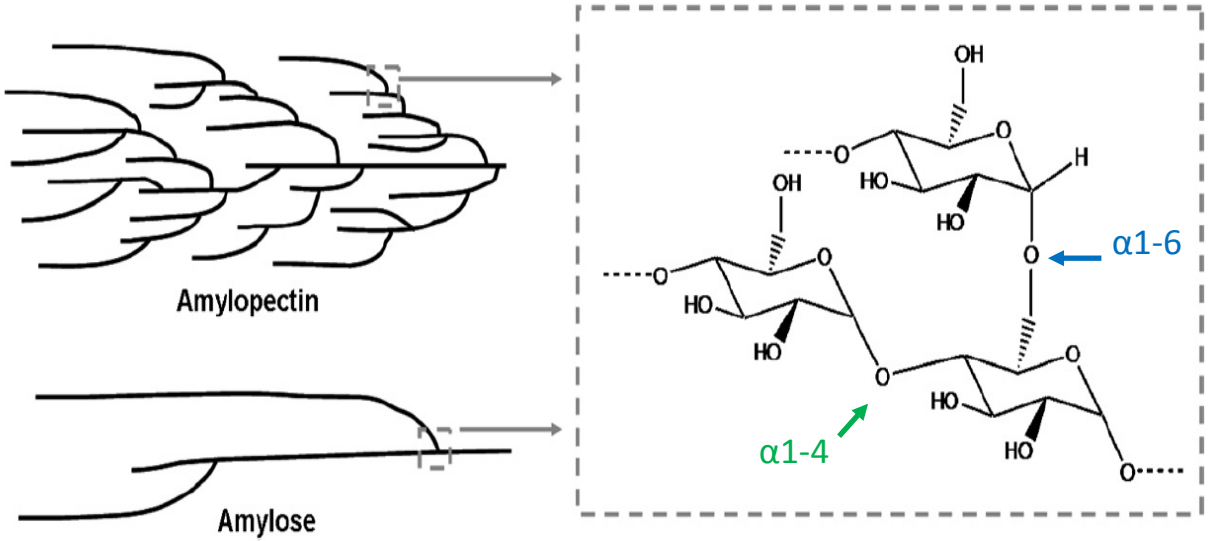
*10mol% free SG1 added

[M]	Time to make 60% starch hybrid
0.64M	43 min
0.19M	100 min
0.08M	105 min

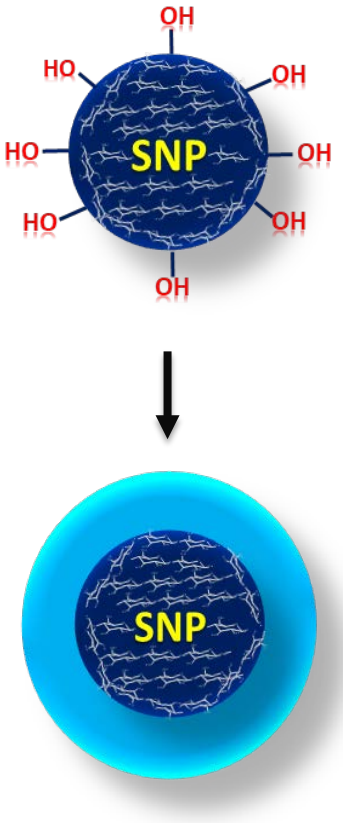




Starch and SNPs (Starch Nanoparticles)



Amylose and amylopectin schematic structural and chemical composition.[2]



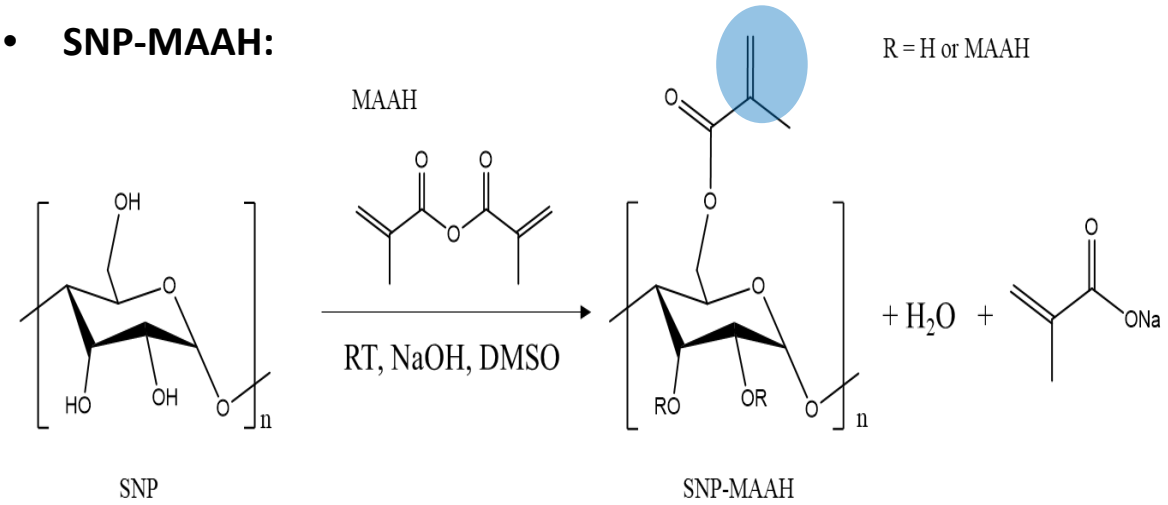
Starch (amylopectin) —*crosslinking agent*→ **Starch nanoparticles (SNPs)**

[2]M. C. Sweedman et al., Carbohydrates Polymers 92 (2013) 905-920.

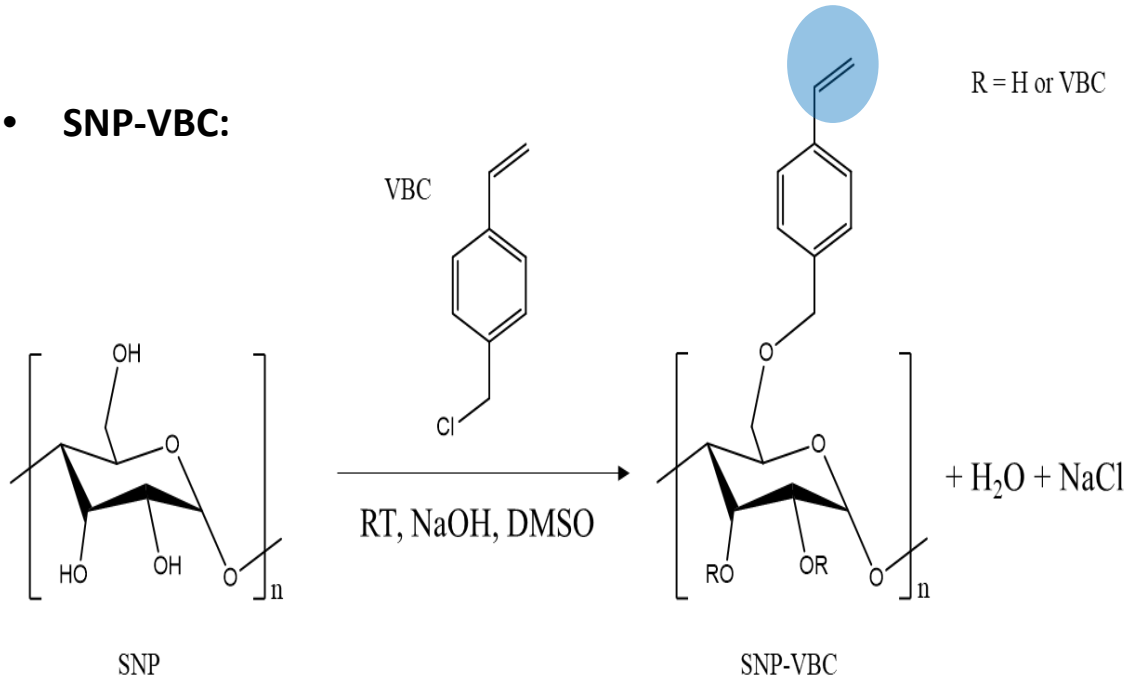
Functionalization of SNPs

1

- **SNP-MAAH:**



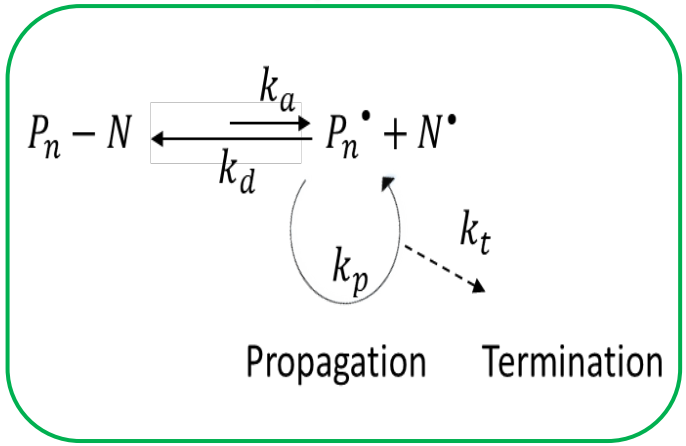
- **SNP-VBC:**



2

Double bond to react with BB and perform NMP

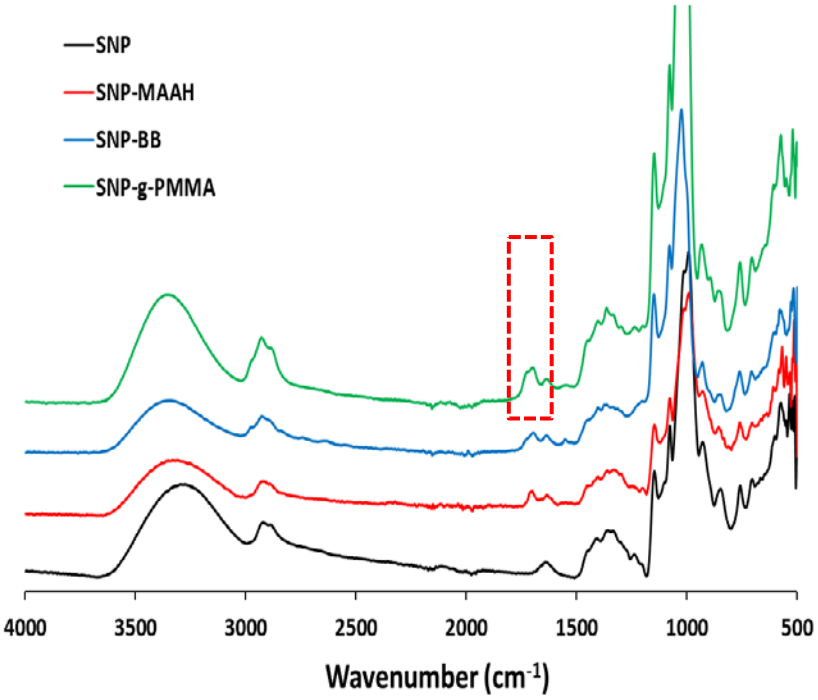
3



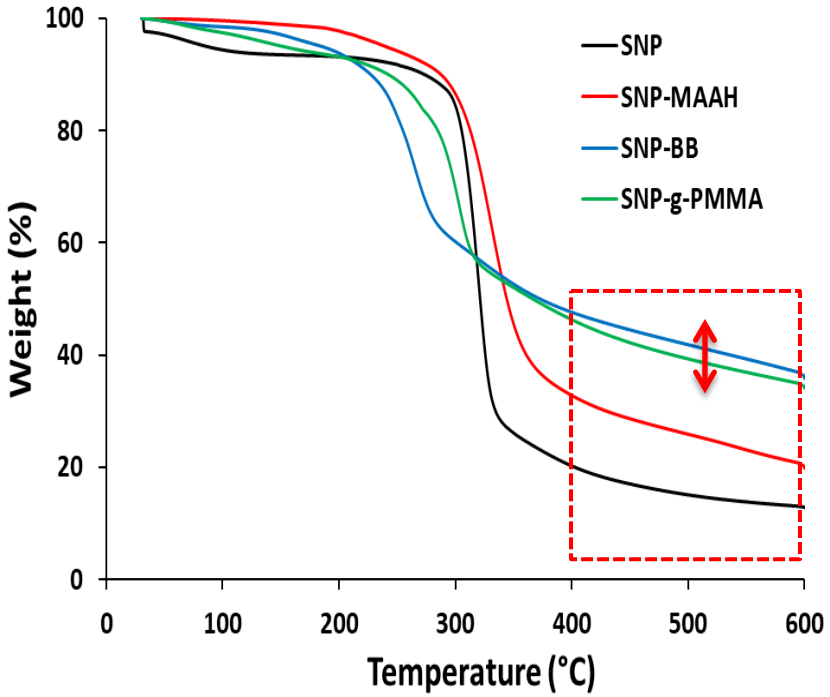
NMP mechanism.

Grafting from SNPs with Methyl Methacrylate (MMA)

MAAH approach:



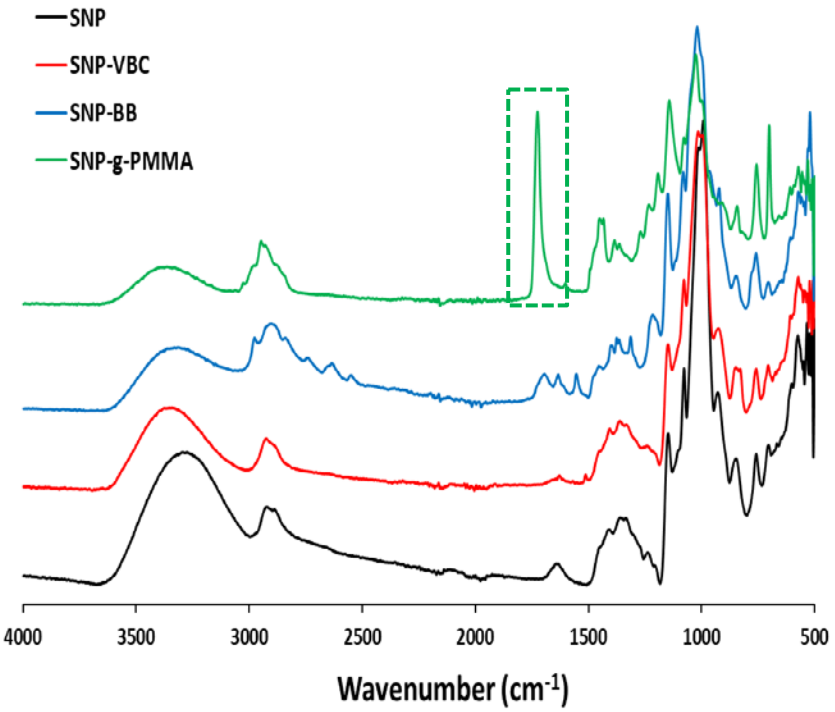
FTIR spectra of SNP-g-PMMA.



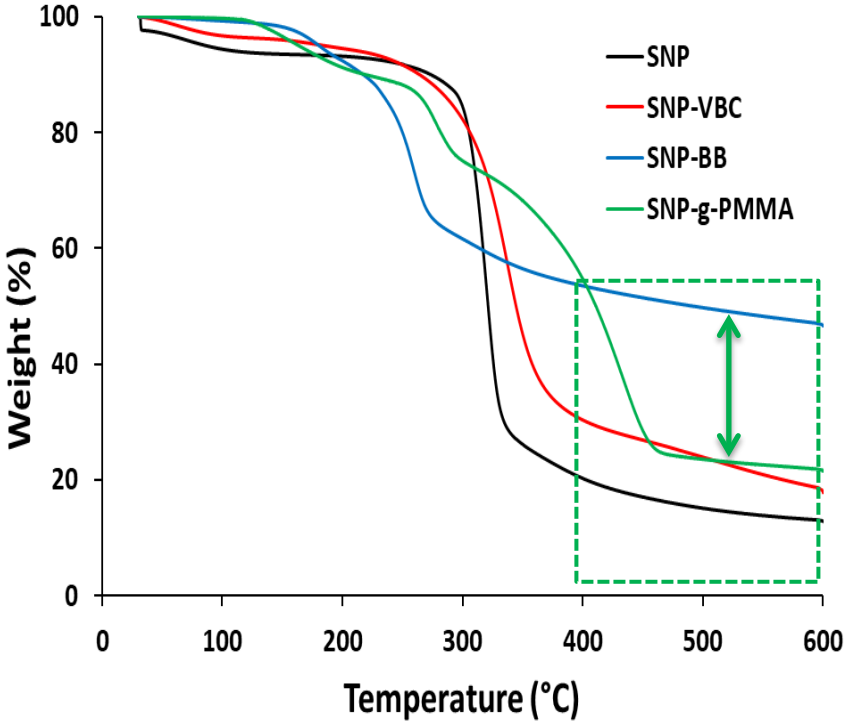
TGA of SNP-g-PMMA.

Grafting from SNPs with Methyl Methacrylate (MMA)

VBC approach:

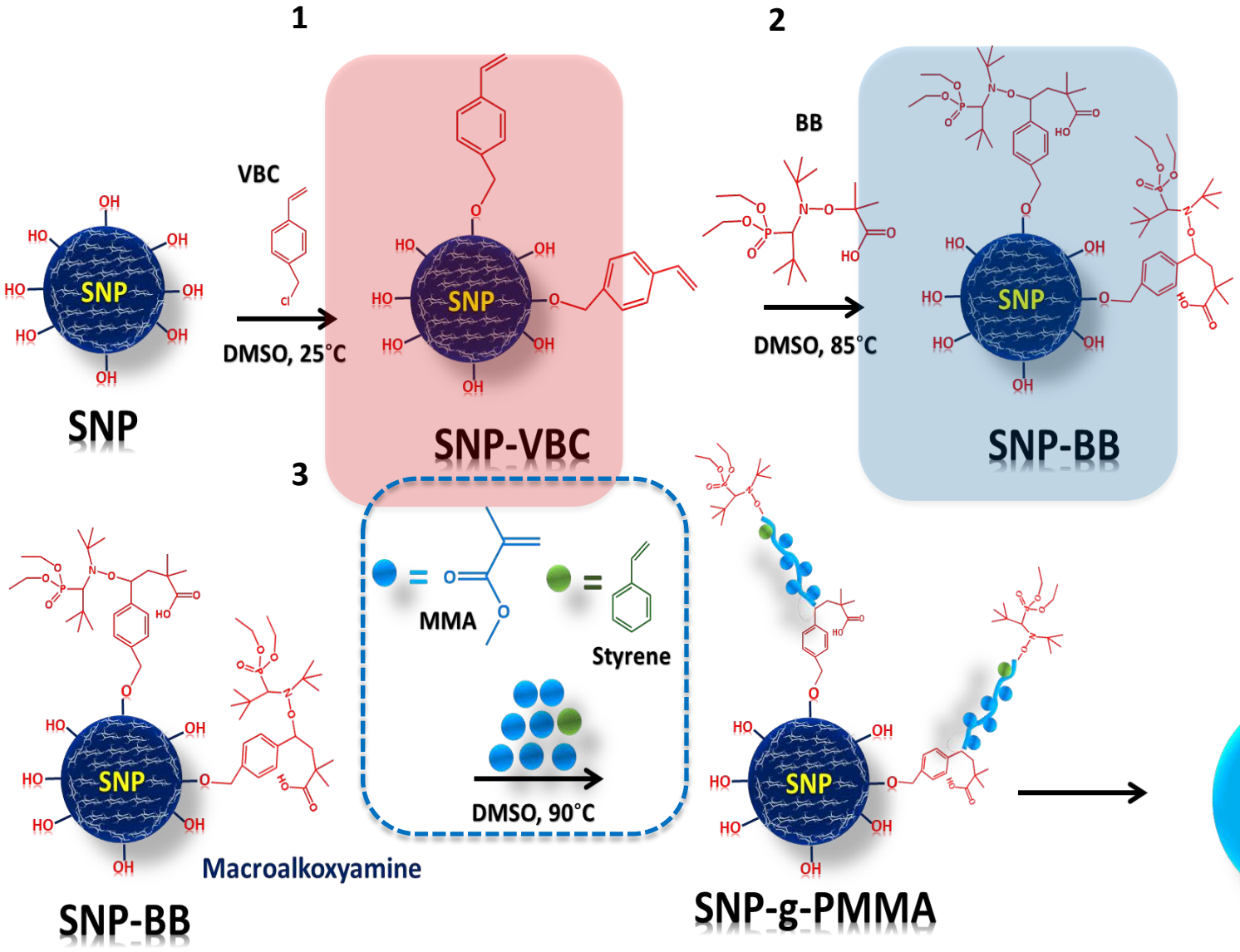


FTIR spectra of SNP-g-PMMA.



TGA of SNP-g-PMMA.

Grafting from SNPs with Methyl Methacrylate (MMA)

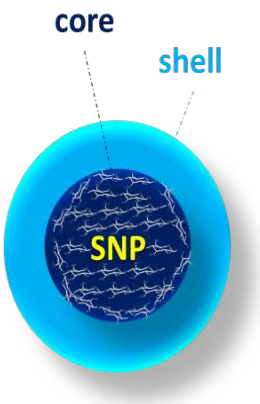


NMR

DS = 0.135

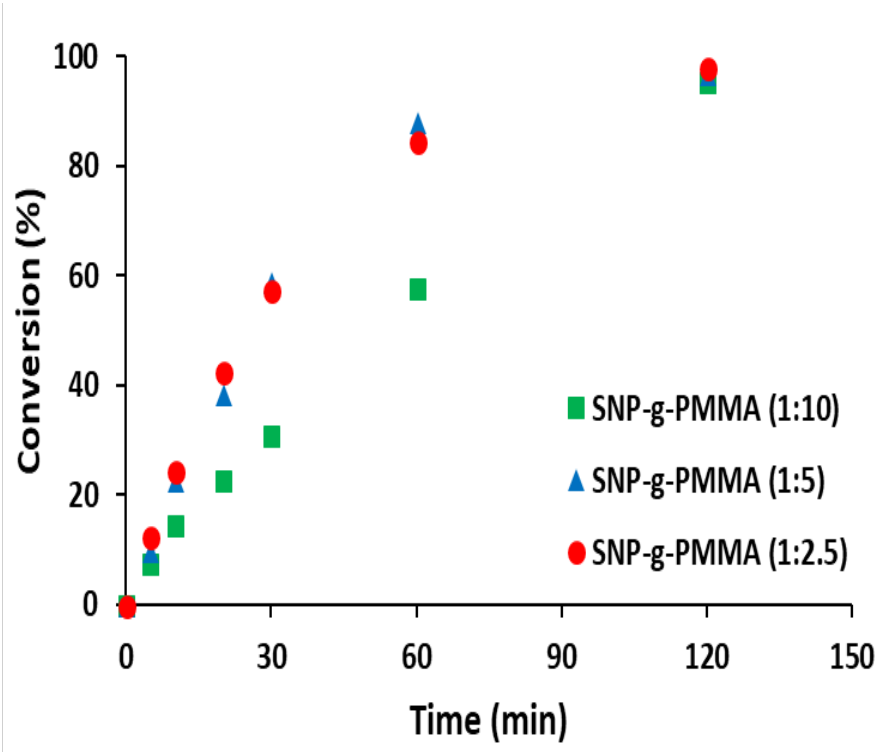
[N] = 0.67%

EA

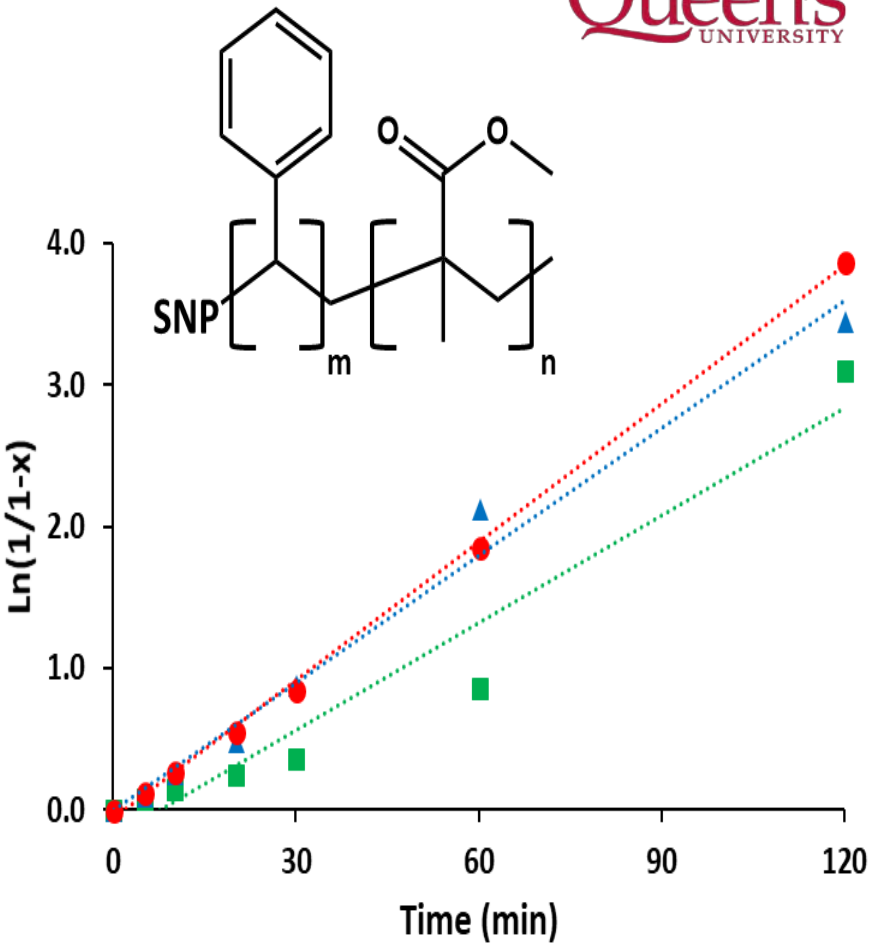


Grafting from SNPs with Methyl Methacrylate

Reaction kinetics:

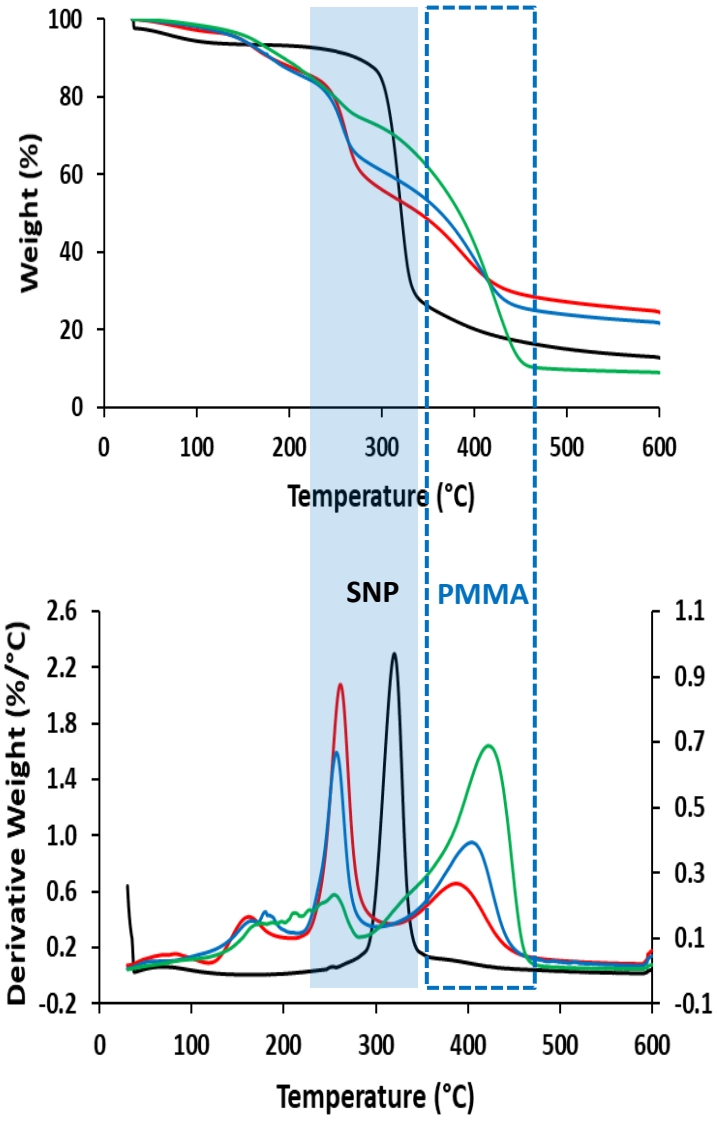


Conversion versus time for SNP-g-PMMA.

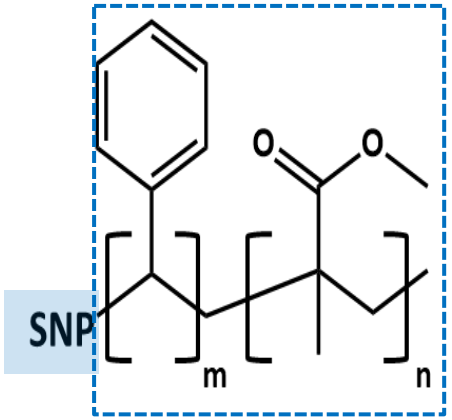


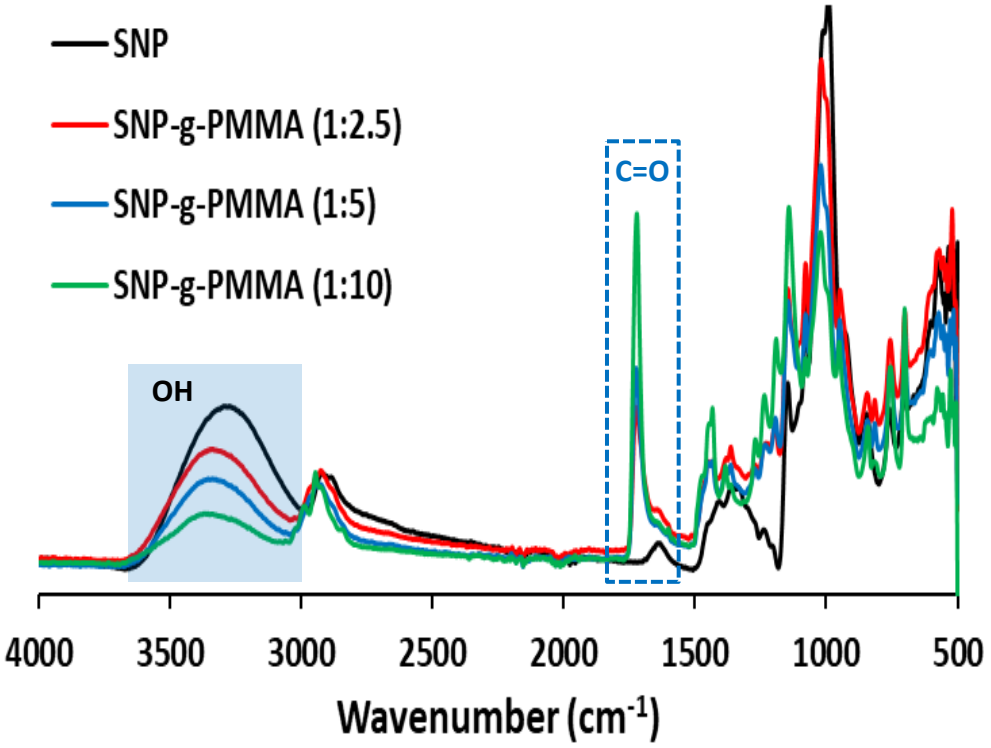
Ln(1/1-x) versus time for SNP-g-PMMA.

SNP-g-PMMA



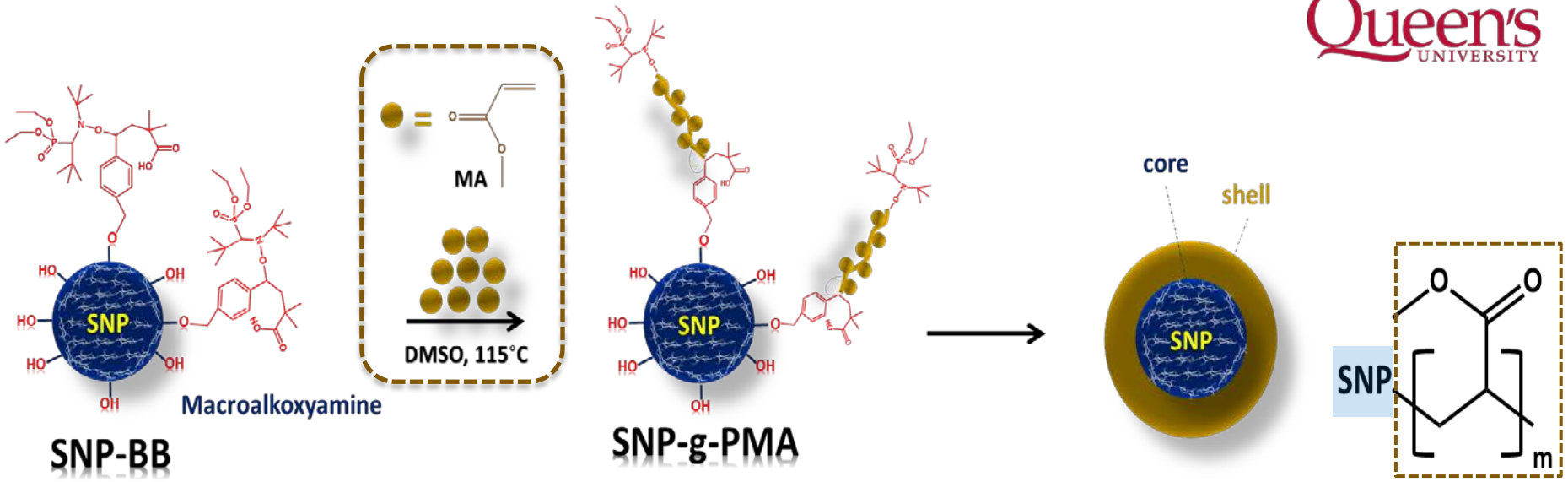
TGA of SNP-g-PMMA.

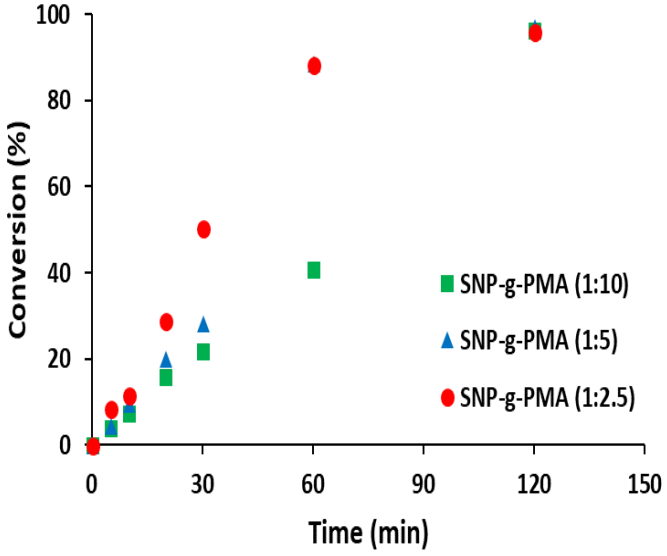




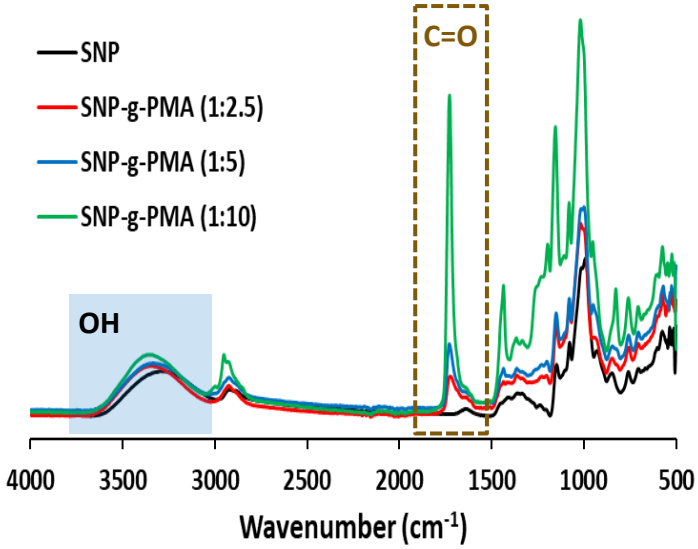
FTIR spectra of SNP-g-PMMA.

Grafting from SNPs with Methyl Acrylate (MA)





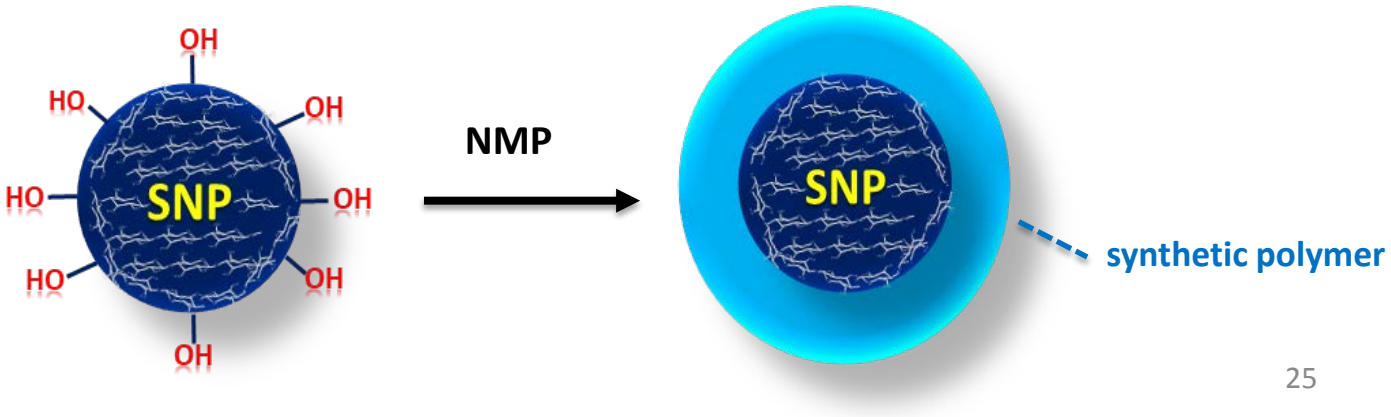
Conversion *versus* time for SNP-g-PMA.



FTIR spectra of SNP-g-PMA.

Summary

- Acrylic polymers can be grafted from starch using NMP
- Reaction time can be used to tune composition of hybrid product
- Functionalization of starch nanoparticles (SNPs): SNP-macroinitiator prepared with BlocBuilder® MA
- **First successful NMP of CWS and SNPs with synthetic polymers**
- Future work: Stimuli-responsive starches



Acknowledgements

NSERC
CRSNG



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