Hydrogen-Bonded Polyaramid Brush Growth on Silica Surfaces

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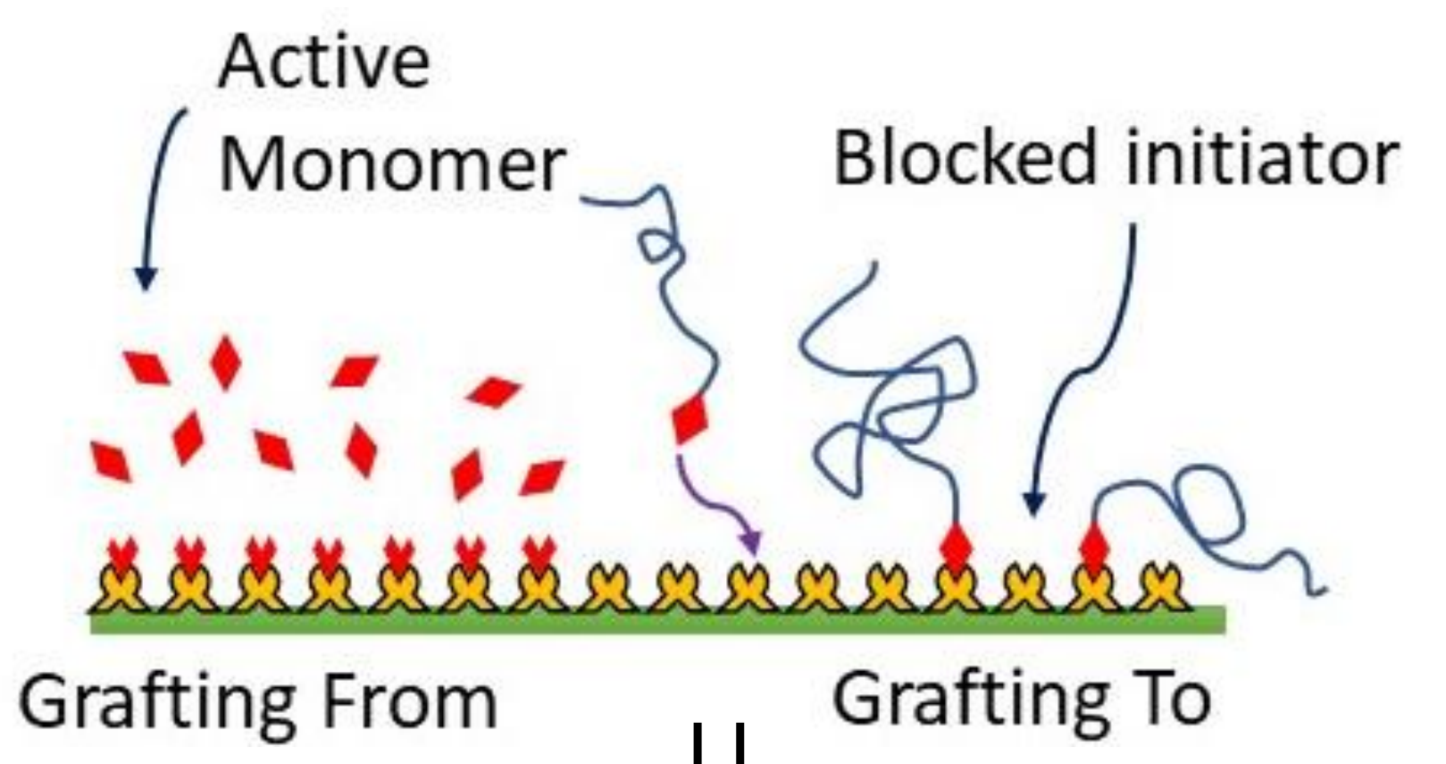
Abstract

Polyaramid brushes are polymers that are grown covalently from a surface yielding a durable coating similar to Kevlar© but at a fraction of the size. Polymer brushes were grown on silica wafers using chain growth condensation and then cleaved to display hydrogen bonding between the brushes which created a self healing, durable structure. Three side chains – 4-nonyloxybenzyl (NOB), 4-hexyloxybenzy (HOB), and tertbutyl – were used in polymer brush growth to aid in solubility and were removed from the brushes using trifluoracetic acid or copper triflate to give the amide proton which allows for hydrogen bonding. Kinetic and solubility experiments were used to understand the effect of these functional side chains on growth rate, molecular weight, and molecular weight distribution. The tert butyl side chain showed the fastest kinetic rate for the phenol monomers at a k_p of 10.4 $s^{-1}M^{-1}$, but currently the smallest brush growth compared to brush growth of NOB and HOB. These and continued kinetic tests will further determine the best kinetic rate for maximum brush growth for the most efficient and durable polymer brushes.

Background

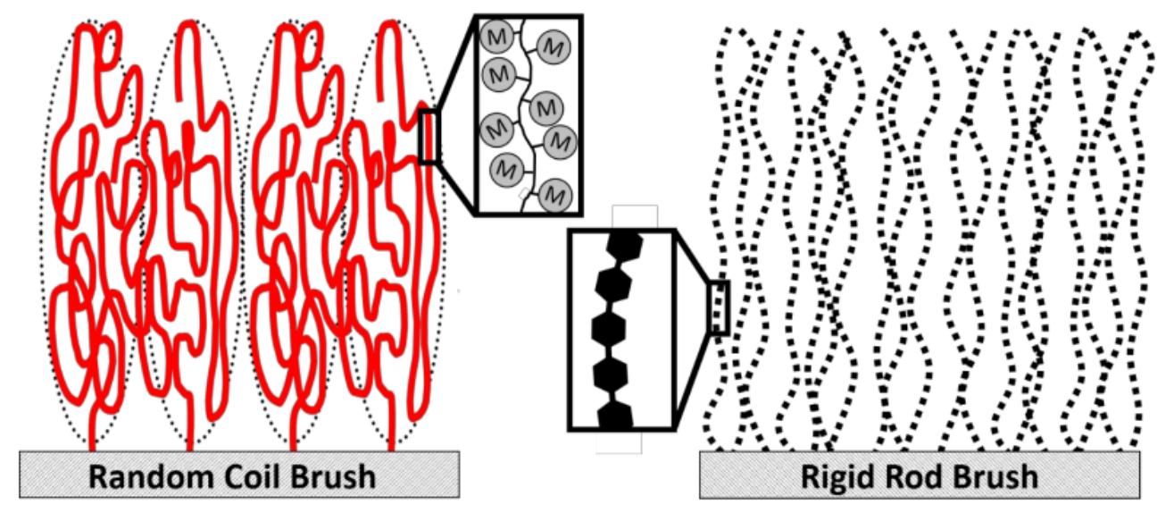
Polymer brushes are polymer chains attached covalently to a surface.



Grafting From
- Use Chain Growth
- Attain predictable Mn
- Higher grafting density

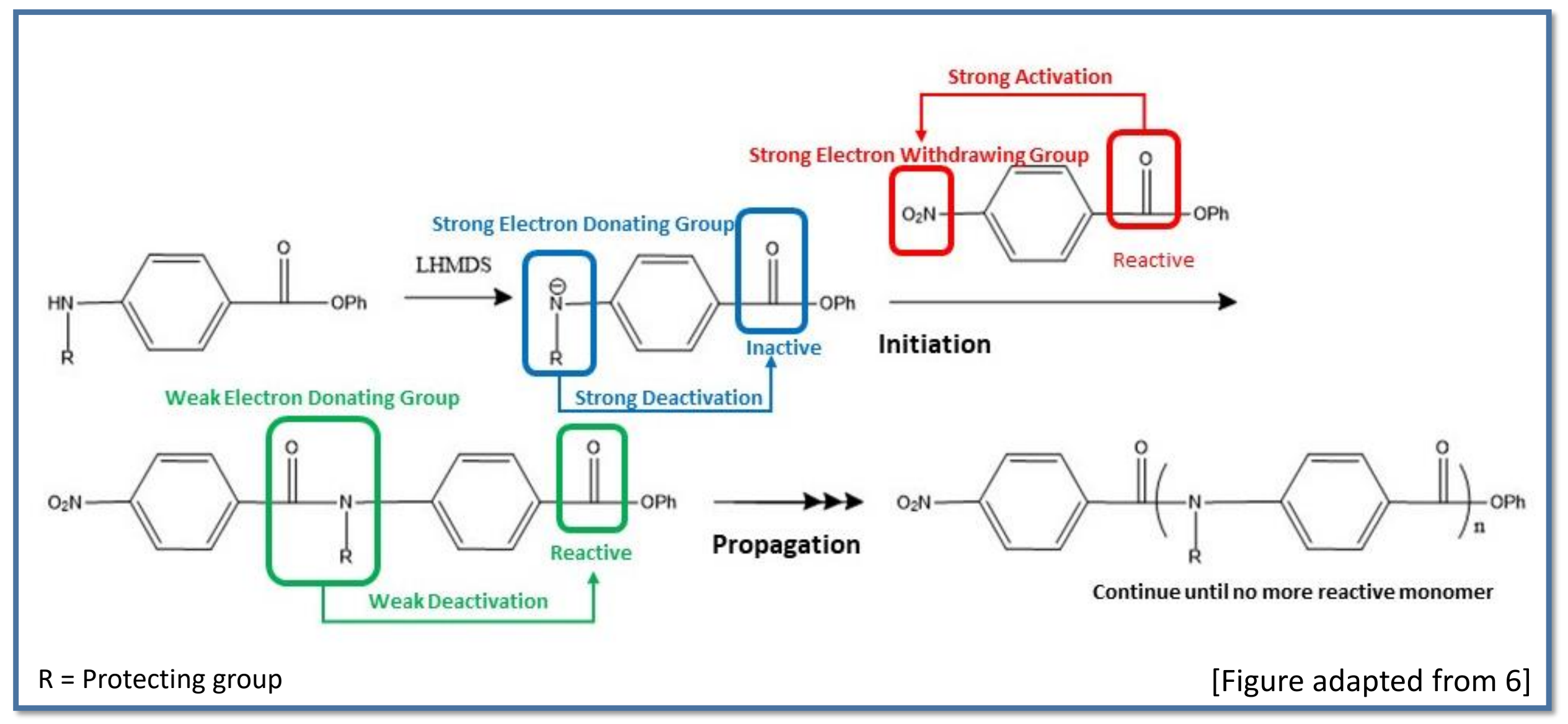
Grafting To
- Use a variety of living polymerization techniques
- Low grafting density

Aromatic rigid rod ideally creates more thermally durable brushes and more brush interaction



Overarching Project Goal: To create durable surface coatings using polyaramid brushes

Polymerization Using Chain Growth Condensation

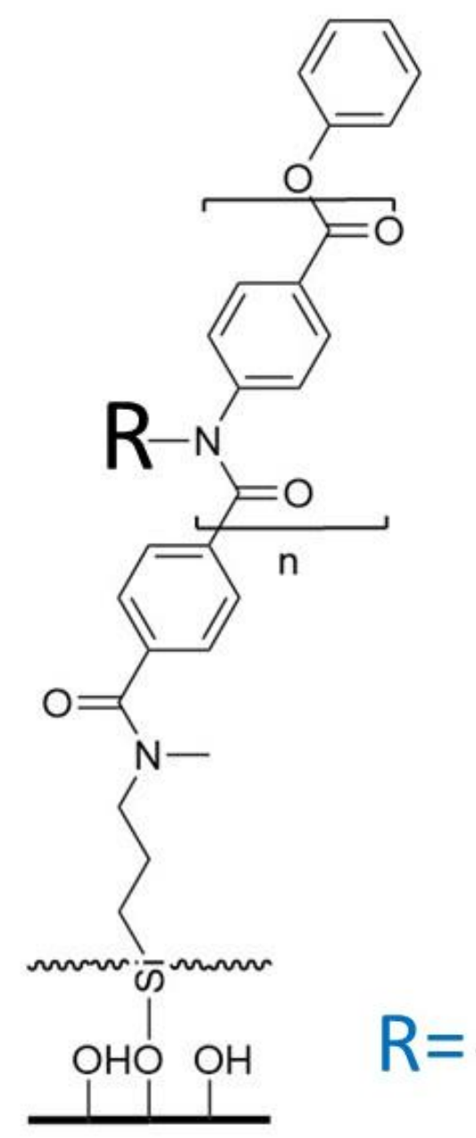


R = Protecting group

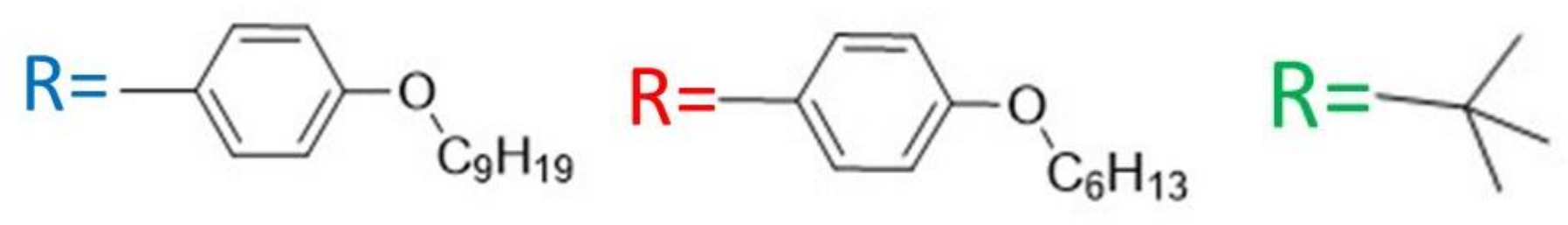
[Figure adapted from 6]

- Activates end of monomer: no self initiation
- Able to reinitiate with addition of more base and monomer
- "Grafting From" ability: Can grow off of a surface
- Creates Rigid Polymer backbone

Protecting the Polymer

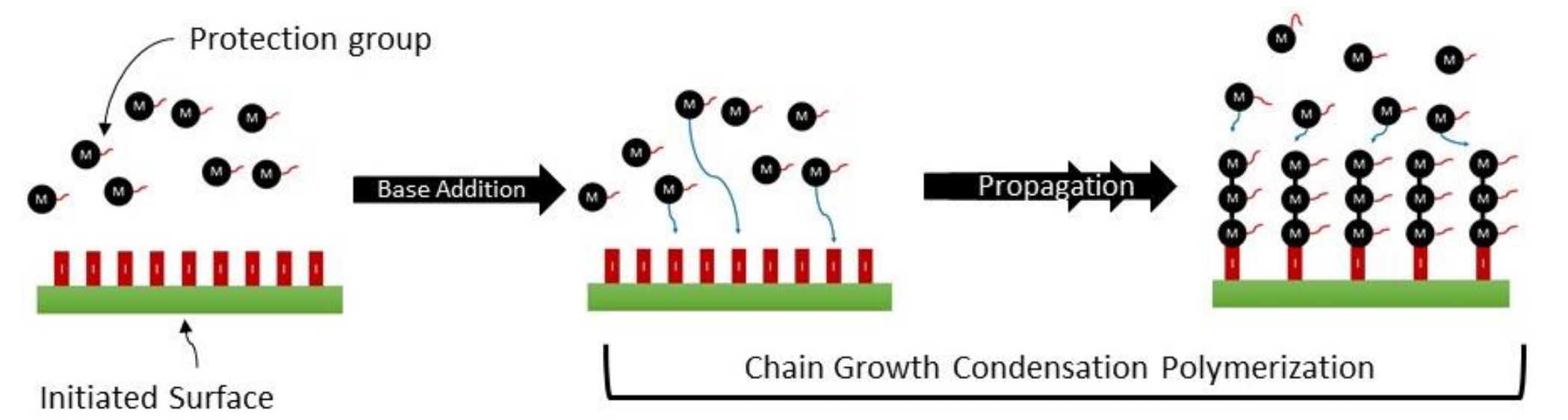


- Increase solubility of brush by adding a more soluble side chain
- Chain can be removed to allow hydrogen bonding
- Side chains can effect polymerization rate and solubility, changing the performance of the reaction



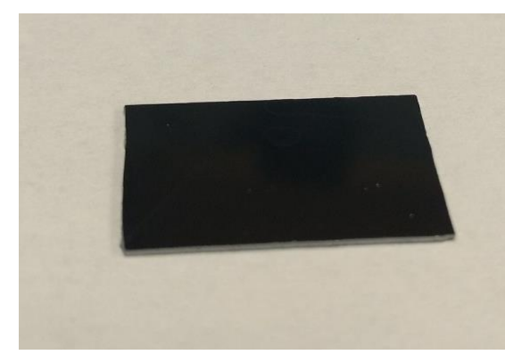
4-Nonyloxybenzyl (NOB) 4-Hexyloxybenzyl (HOB) tert butyl

Growth of Polymer Brushes



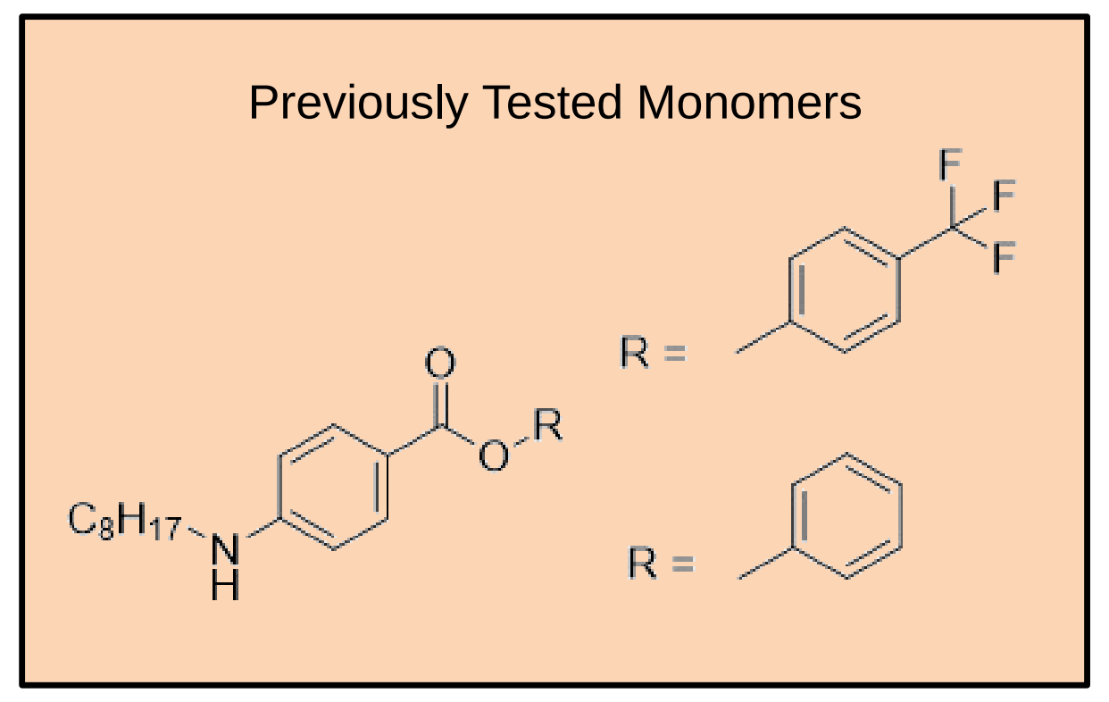
- Growth effected by: Temperature, Monomer and Solubility

Brushes are grown on 2 cm by 1 cm silica wafers

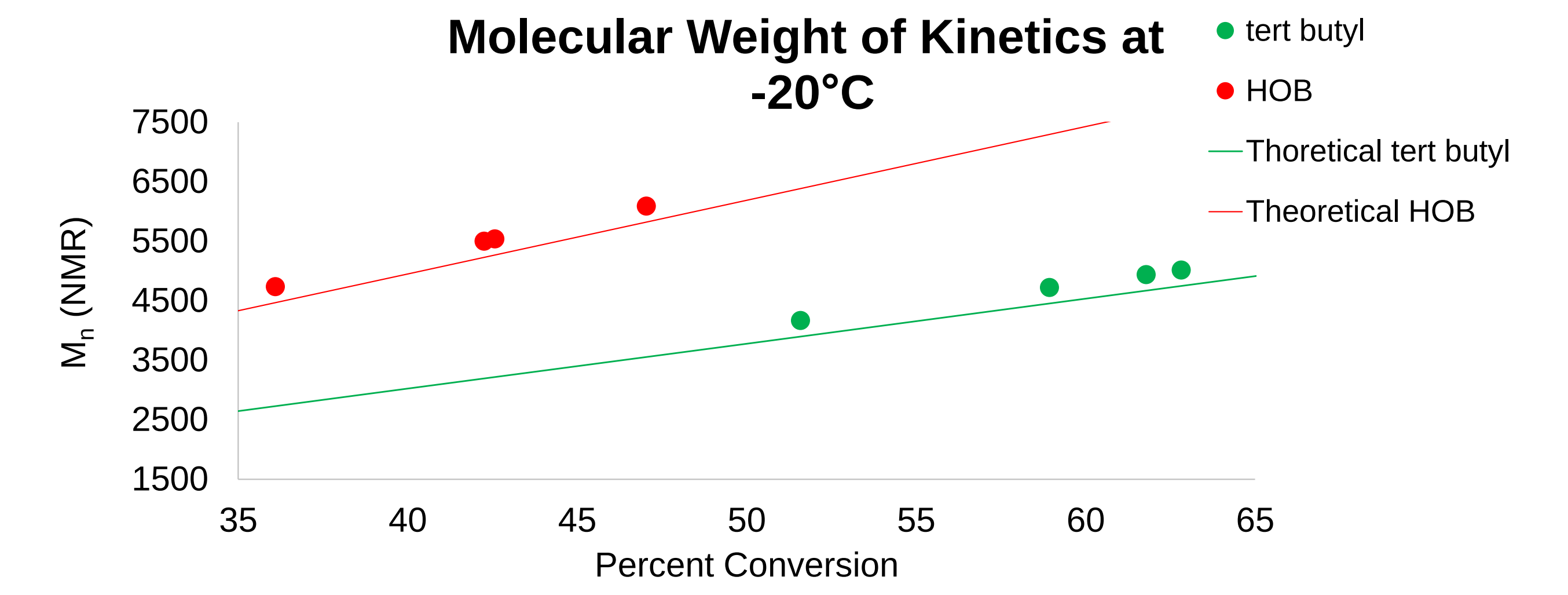


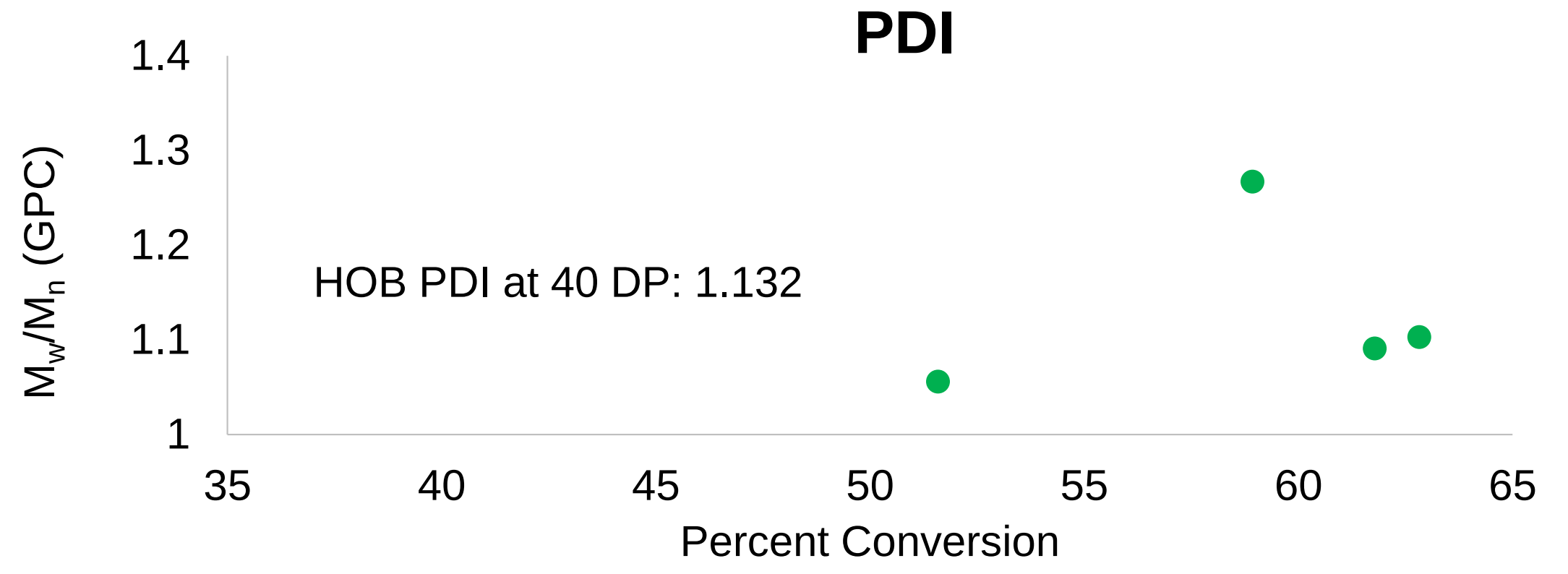
Brush Growth on Silica Wafers	
Side Chain	Growth Length
HOB	24.269±0.0289 nm
NOB	48.152±0.293 nm
tert butyl	9.04±0.37 nm

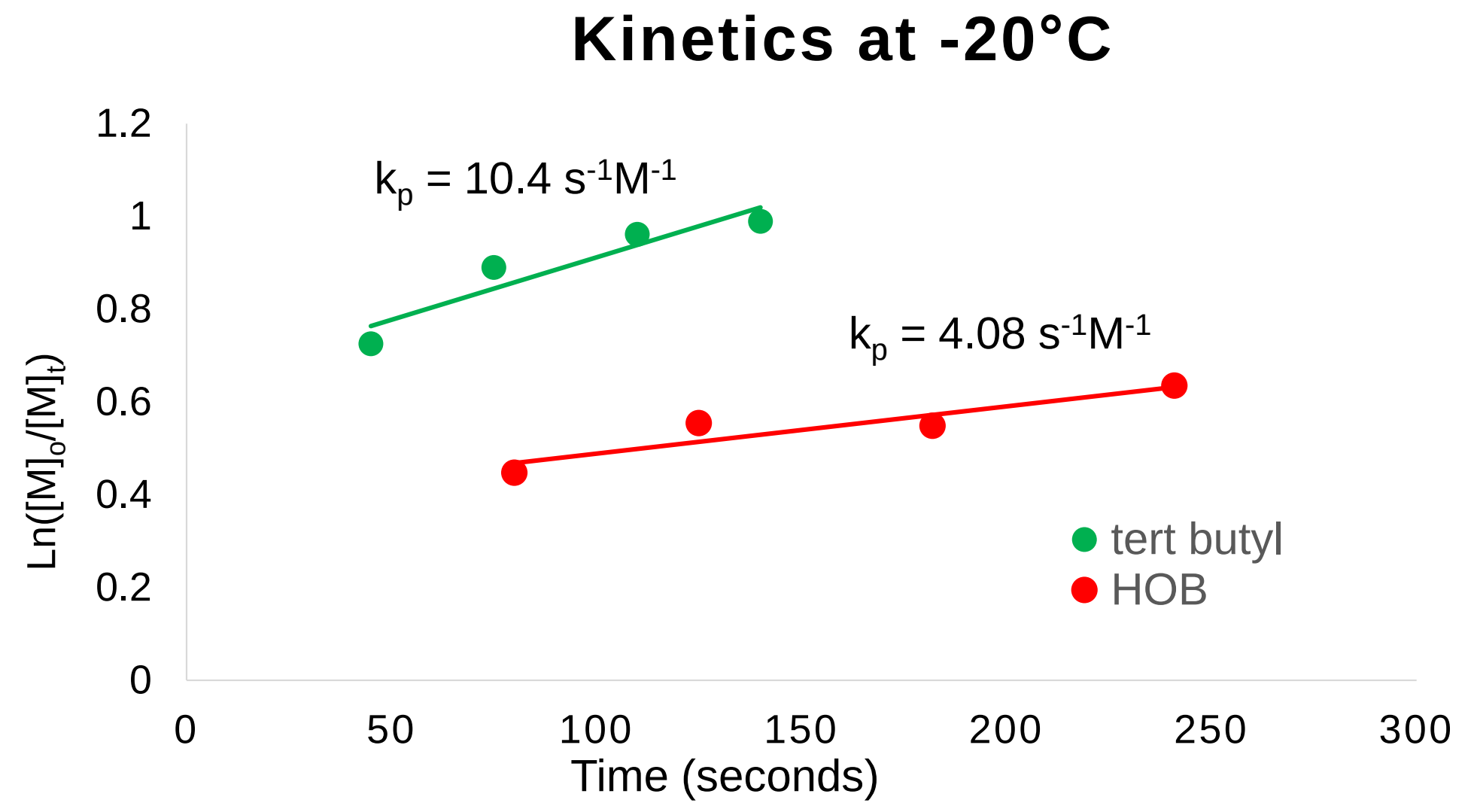
Addressing the Kinetics



- Previous kinetic data for different monomer leaving groups was conducted using an octyl side chain





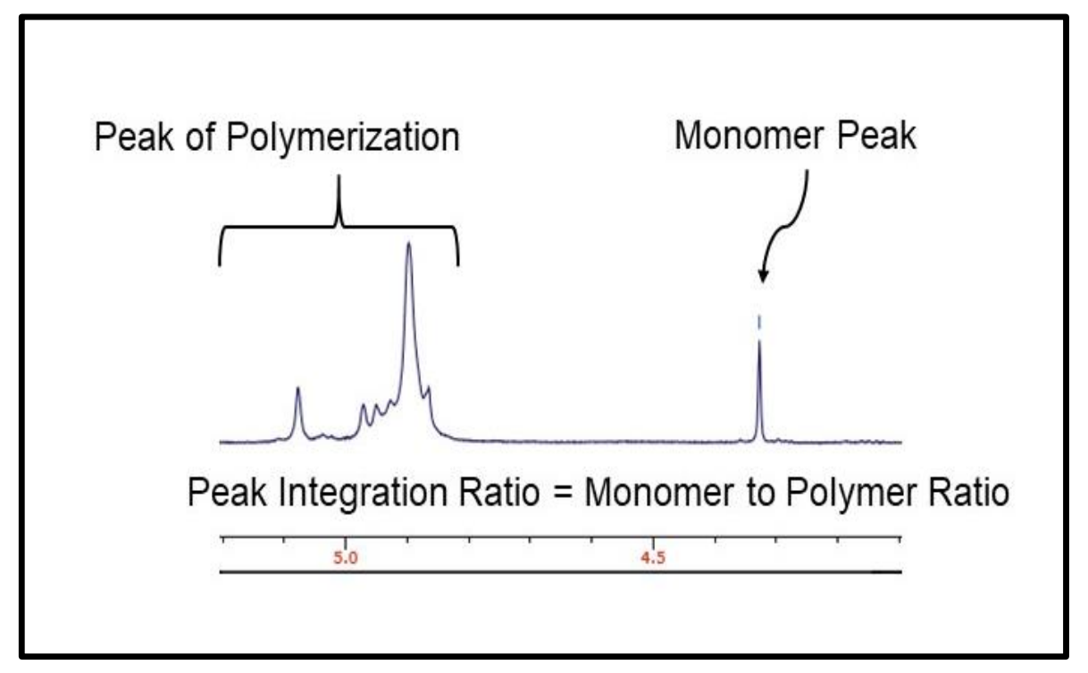


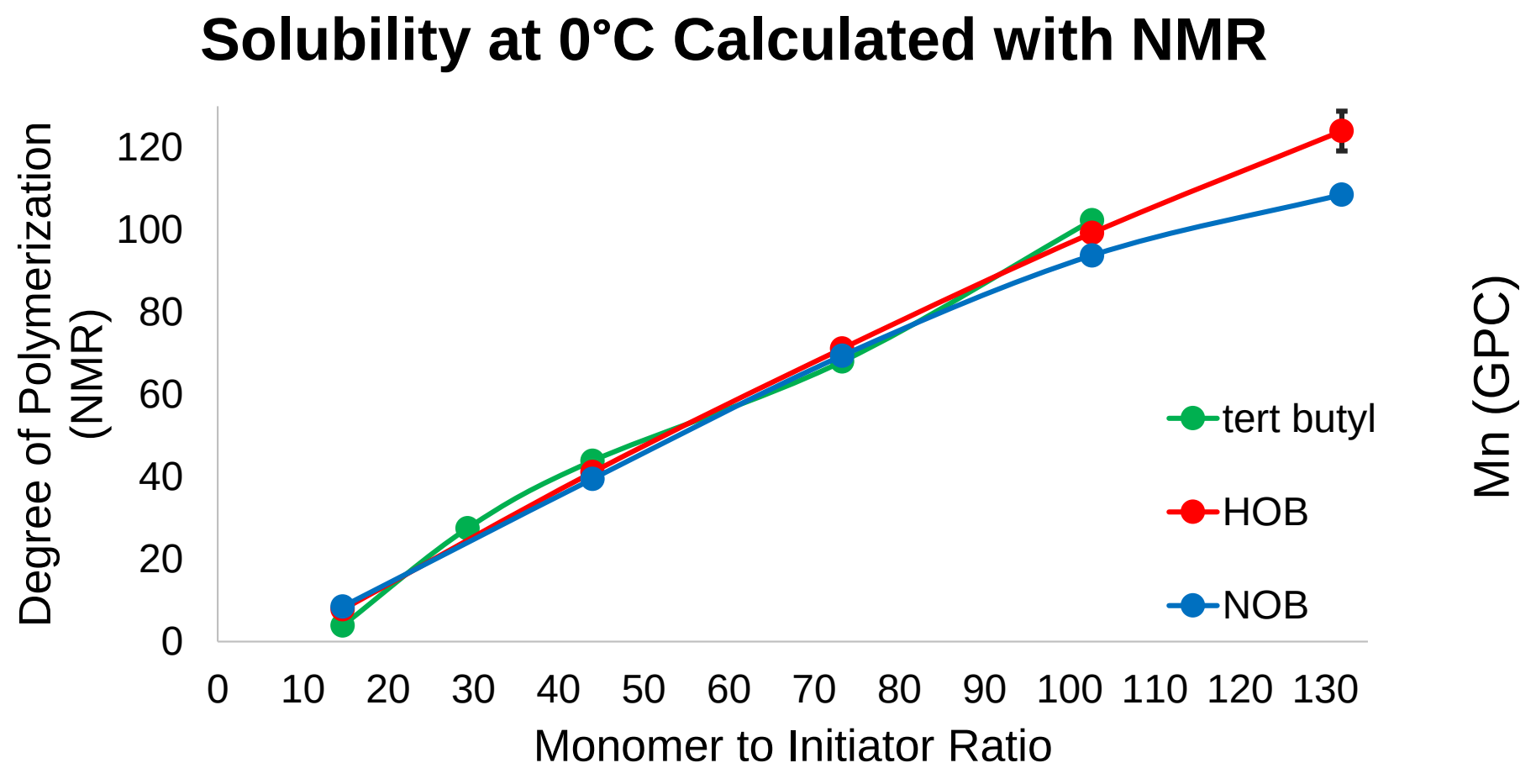
$$\ln\frac{[M]_0}{[M]_t} = k_p [I]_0 t$$

Kinetics of Different Monomers		
Monomer	Side Chain	k_p (s^{-1})
Phenol	Tert Butyl	10.4
Phenol	HOB	4.08
Phenol	Octyl	0.64
Trifluoro Methyl Phenol	Octyl	14.3

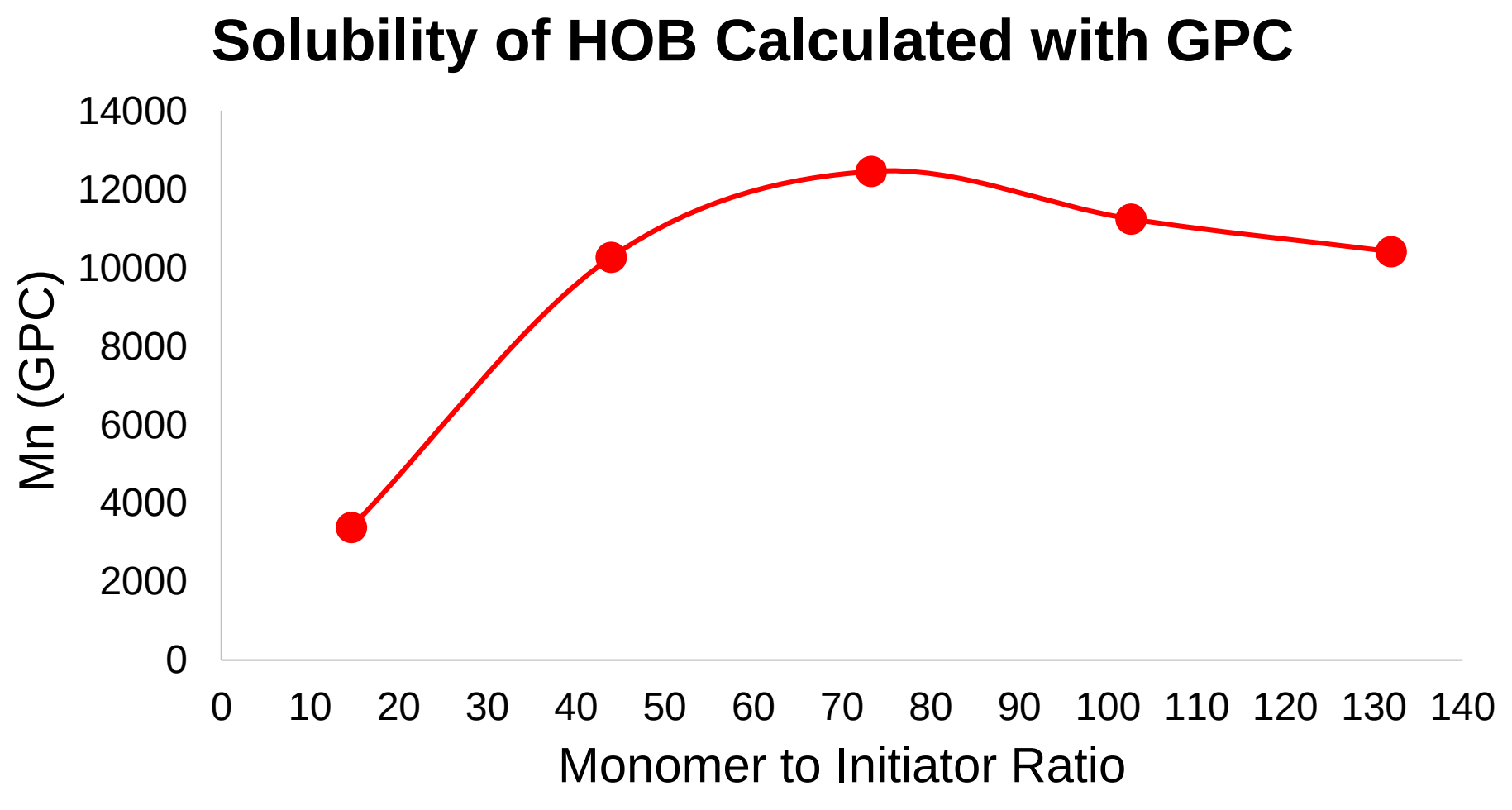
Understanding The Solubility

Solubility tests are performed with varying ratio of initiator to monomer to test how long the polymer can grow before falling out of solution in tetrahydrofuran (THF) solvent.



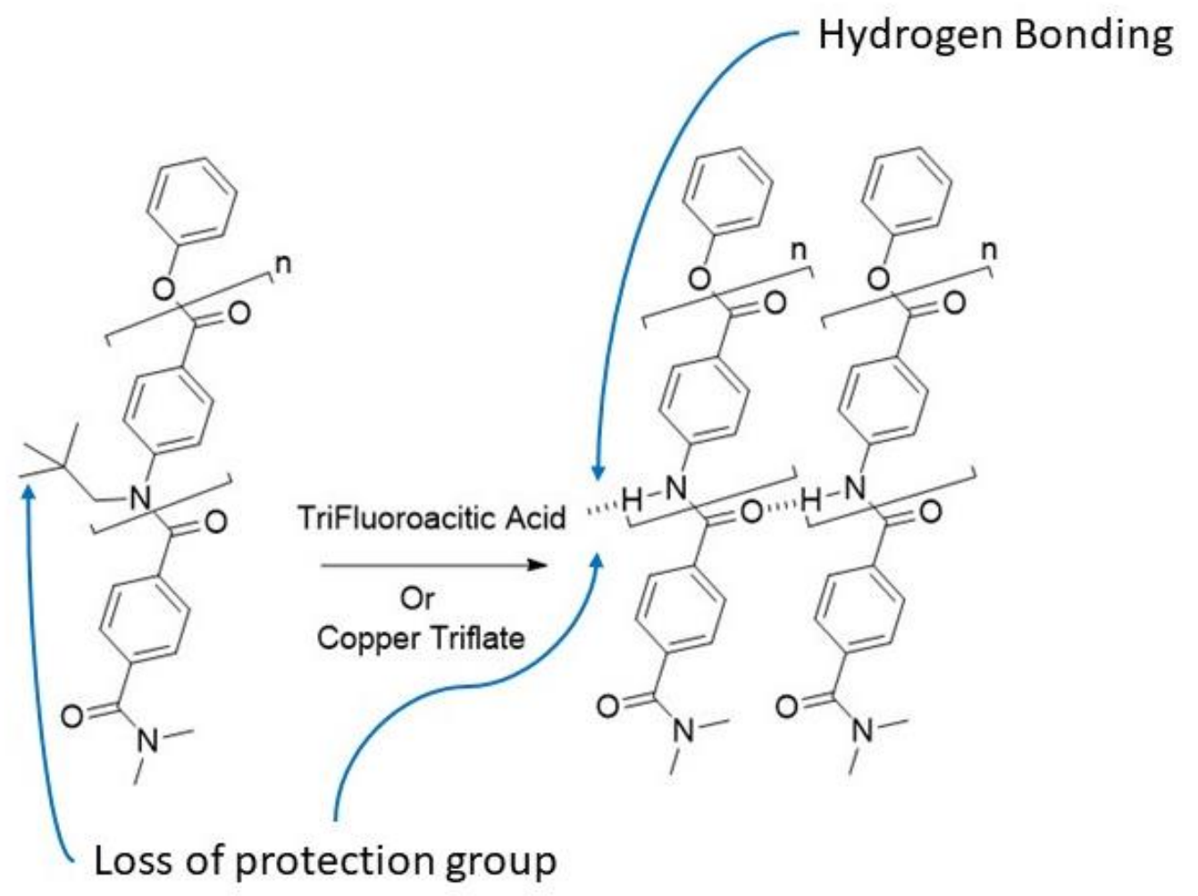


- NMR cannot differentiate between self-initiated polymerization, so GPC is needed to verify solubility.



- The GPC (Gel Permeation Chromatography) for HOB is shows chains are not growing longer than 70 monomers, which gives a better understanding of the polymer's solubility

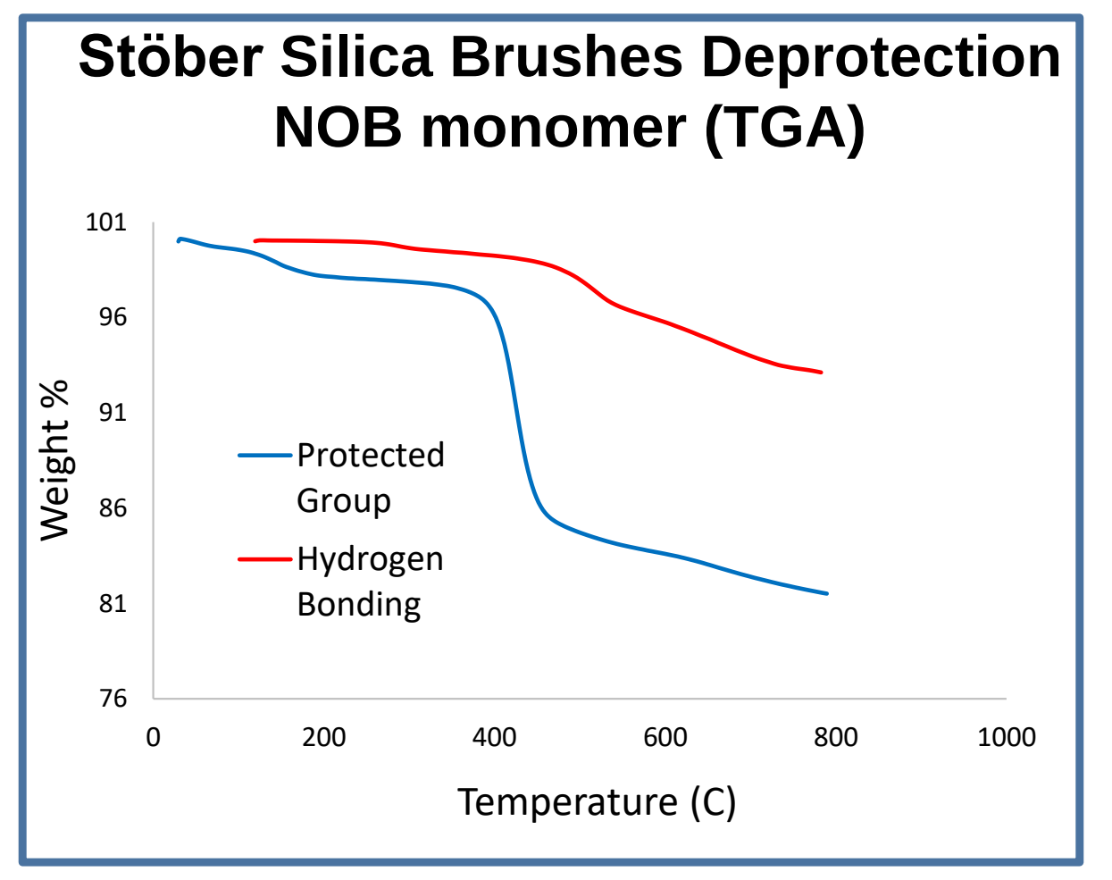
Cleaving the Protection Group

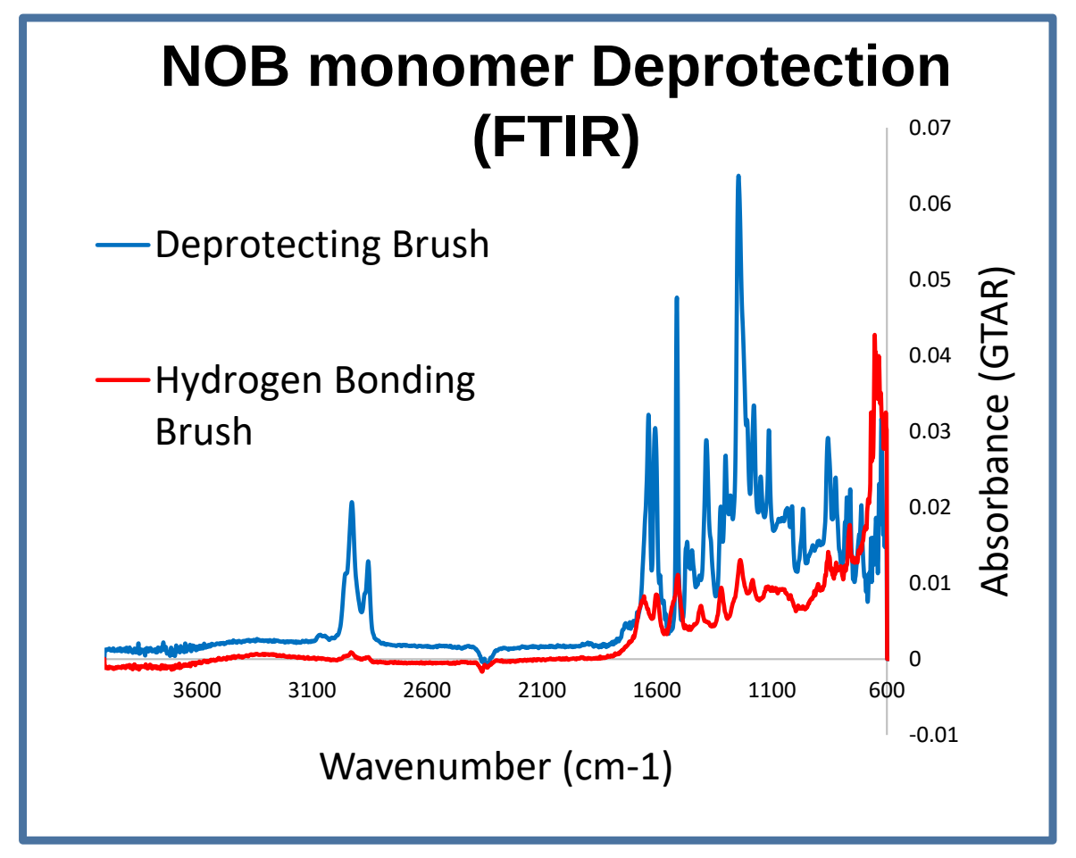


The deprotected brush displays hydrogen bonding, which (similar to Kevlar) is expected to have qualities of:

- High temperature resistance
- Self-healing abilities
- Absorption of force

- Hydrogen bonding allows the brush to withstand higher temperatures
- Brushes are formed on 500 nm Stöber and have similar grafting density. They can display polymer burn off amount





- Peak at 3100 cm^{-1} disappears when protection group cleaved
- Similar data collected for tert butyl and HOB protection groups

Conclusions

- The different side chains effects the solubility and kinetic rate of polymer brushes and change the polymerization rate of the phenol monomer.
- All side groups have had some brush growth on both silica wafers and Stöber silica and have been successfully cleaved to demonstrate the hydrogen bonding necessary for durable surface coatings.
- Solubility tests - though currently inconclusive - show potential for understanding different brush growth lengths.

Future Directions

- Further kinetic and solubility tests to determine the best monomer for brush growth
- Adjust methods to increase brush growth on silica wafers by changing reaction conditions and monomer groups
- Conduct durability tests to verify limitations to new surface coatings

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