

# Toward Thermoplastic Lignin Polymers; Synthesis & Analysis

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# Objective

To describe our approach aimed at creating heat stable technical lignin melts

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Aimed at Thermoplastics, Precursor to carbon Fibers & Engineering Heat Stable Polymers

The concerted use of a variety of analytical tools is indispensable in such endeavors

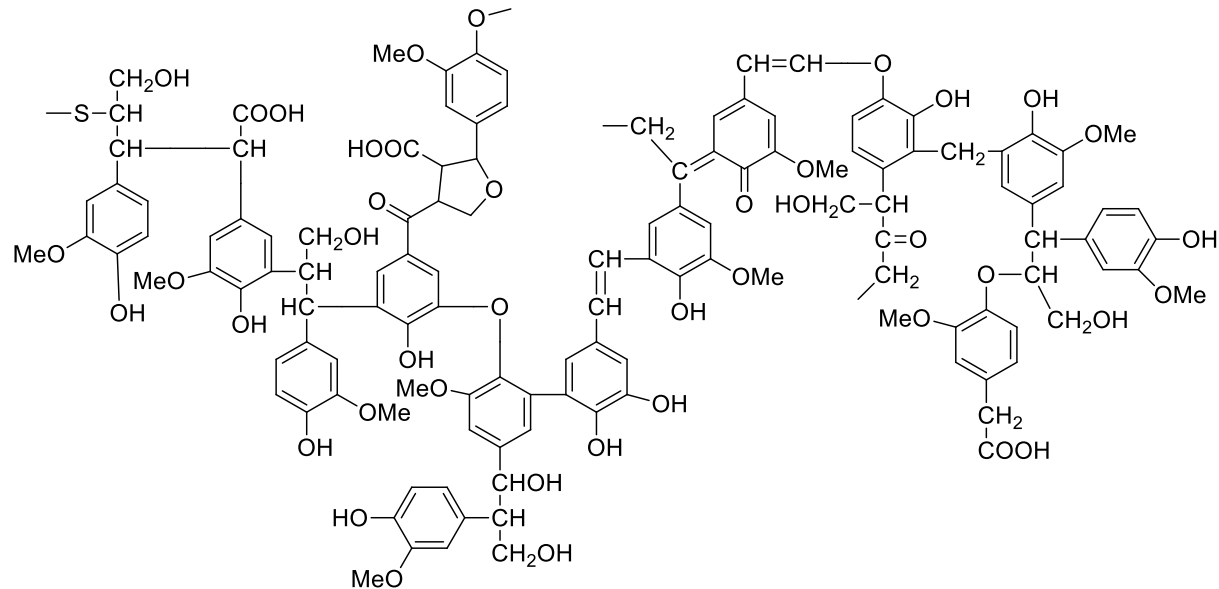
Fundamental Science aimed at Creating  
Thermoplastic Lignin Melts

Defining the Science & a Novel Approach aimed at  
Creating Carbon Fibers from Lignin Melts

Heat Stable Polyarylene Ether Sulfone -Kraft  
Lignin Co-Polymers

# Fundamental Science aimed at Creating Thermoplastic Lignin Melts

# Kraft Lignin Structure In Bad Need for A New Model



*Marton, J. 1971.*

Softwood kraft lignin is highly susceptible to thermally induced reactions that cause its molecular characteristics to be severely altered. These events seriously interfere and prevent such materials from being considered as candidates for thermoplastic applications.

# Effect of Heating on the Molecular Weight Distribution of Underivatized Kraft Lignin

Cui, C., et al. "Toward Thermoplastic Lignin Polymers; Part II:  
" BioResources 8(1), 864-886, (2013).

# Starting Softwood Kraft Lignin "Indulin"

Molecular Weight :

Mw = 8000 (g/mol)

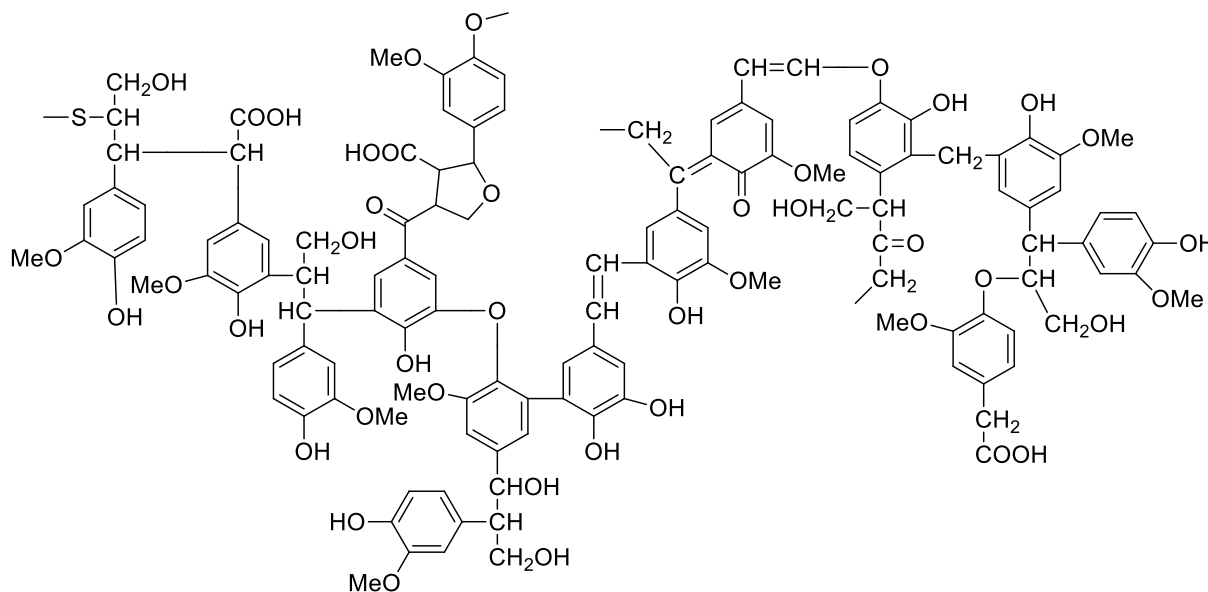
Mn = 2000 (g/mol)

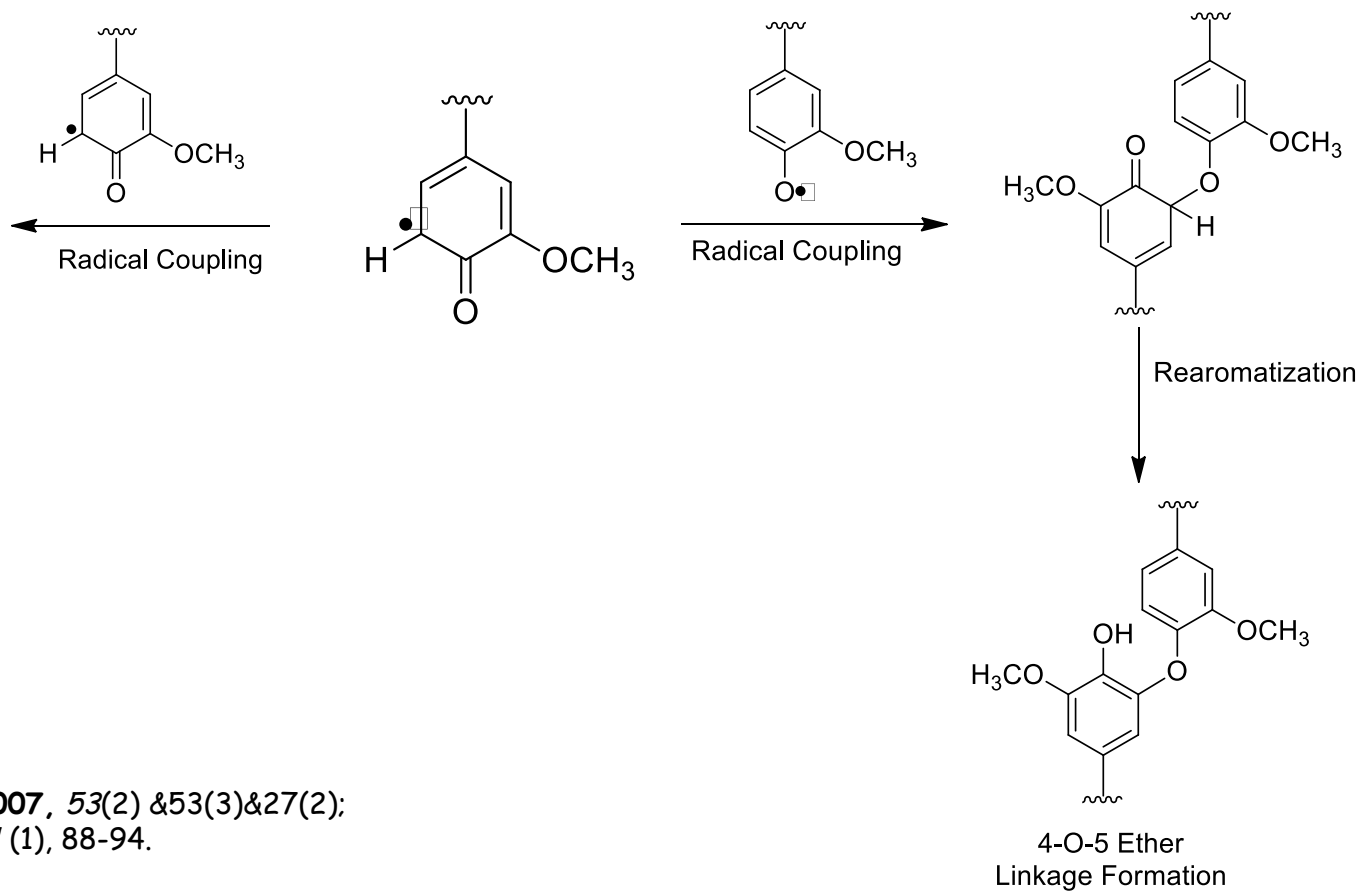
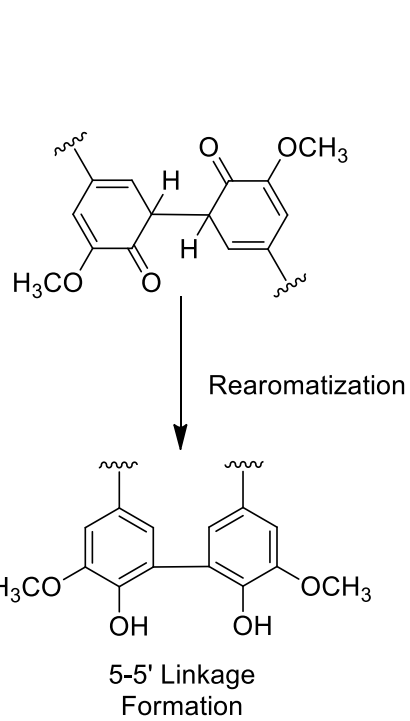
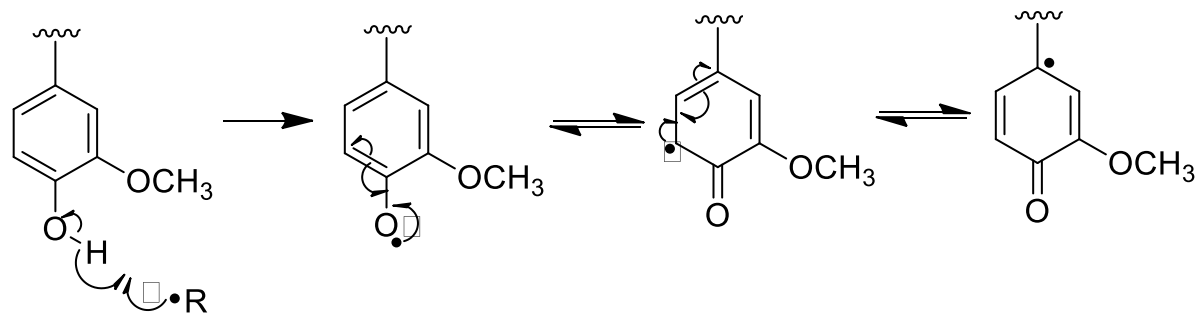
( Mw/Mn = 4 )

Total phenolic-OH = 3.85 mmol/ g

Total Aliphatic-OH = 2.4 mmol/g

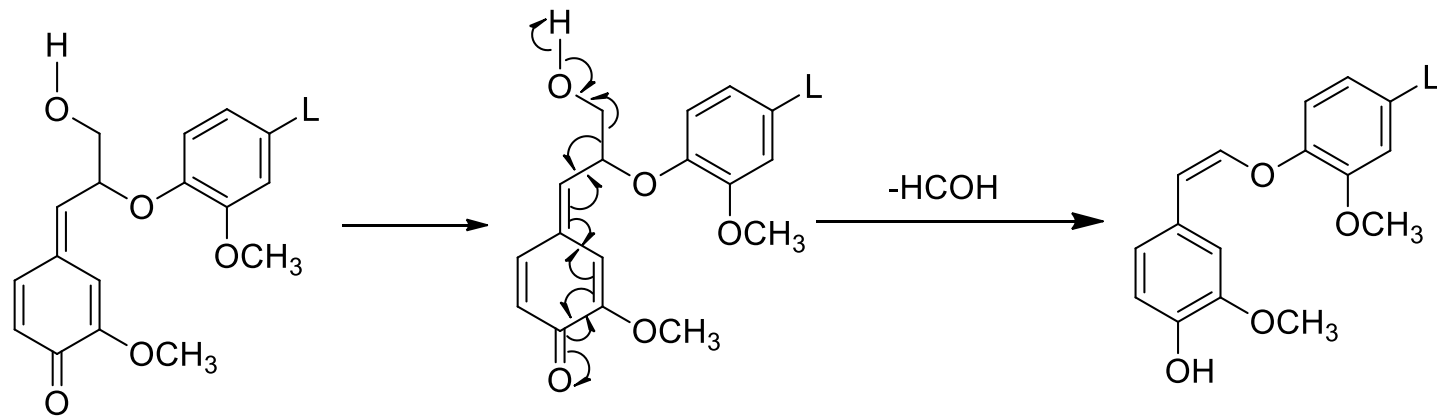
Tg : 150-160°C .



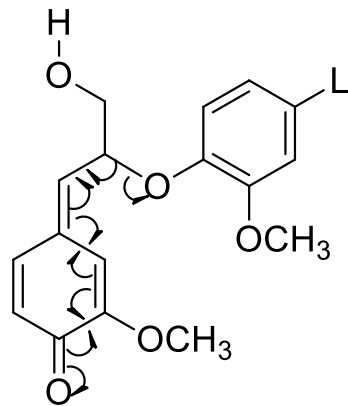


Kawamoto, et al. *J. Wood Sci.* **2007**, 53(2) & 53(3) & 27(2);  
*J. Anal. Appl. Pyrolysis* **2008**, 81 (1), 88-94.  
*Holzforschung* **2008**, 62 (1), 50.  
 Ohashi, et al.. *Org. Biomol. Chem.* **2011**, 9 (7), 2481-2491



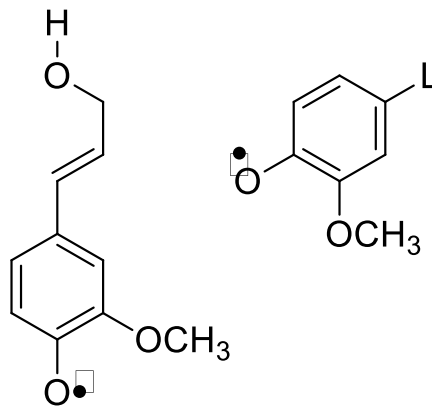


Quinone Methide



Quinone Methide

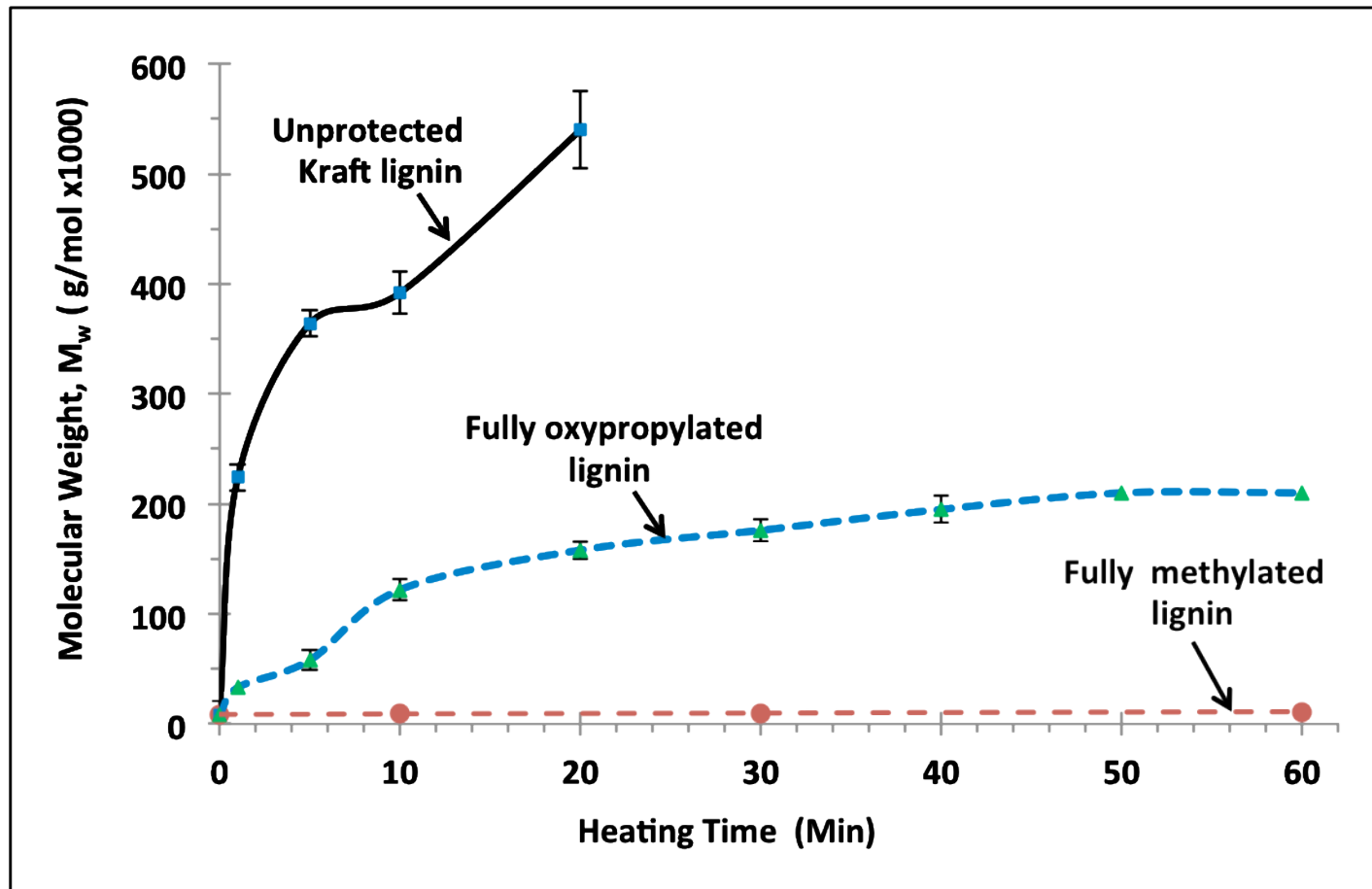
Formaldehyde Generation



Phenoxy Radicals

How does the Phenolic OH  
& its Derivatives Define the Thermal  
Reactivity of Kraft Lignin ?

## Effect of Heating Kraft Lignin & Derivatives 20 °C above $T_g$ on Molecular Weight

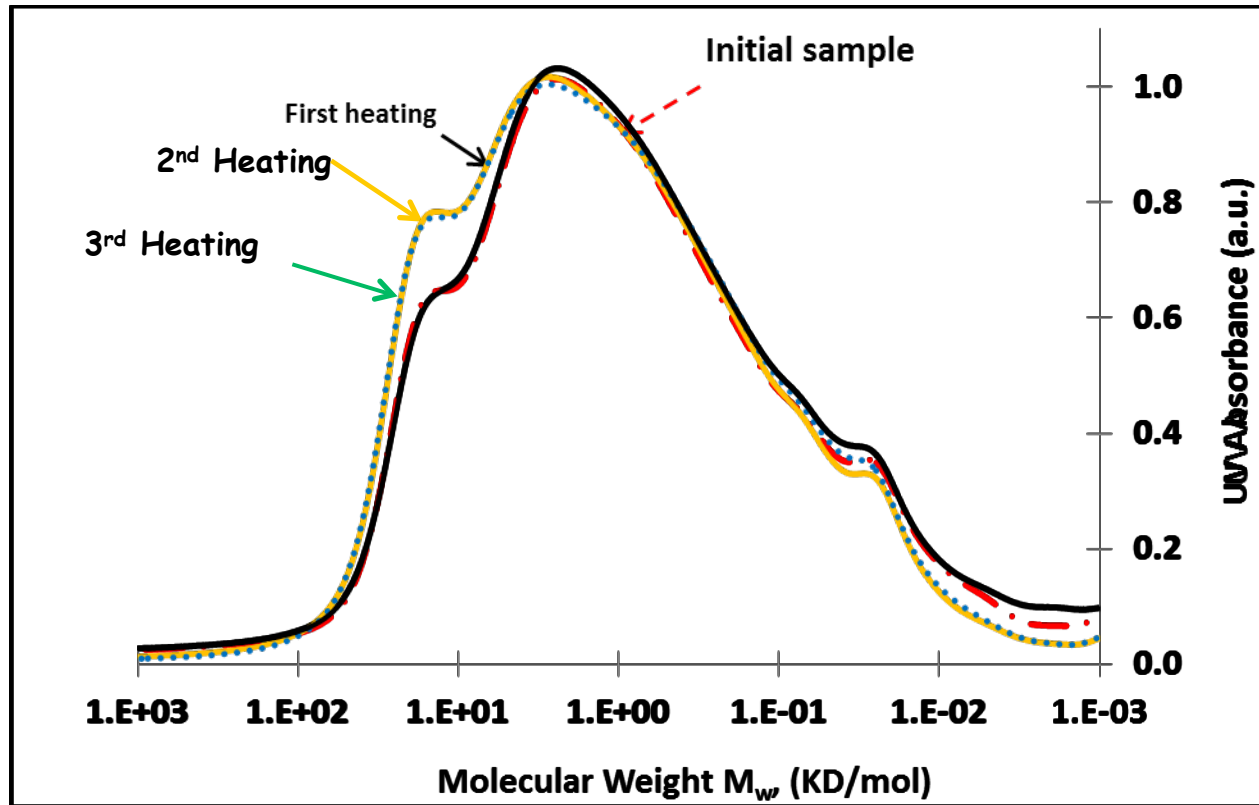


Cui, C., et al. "Toward Thermoplastic Lignin Polymers; Part II: " BioResources 8(1), 864-886, (2013).

Since methylation of the Phenolic OH with Dimethyl Sulfate showed promising thermal stability...

- Is this stability permanent ?
- Can the material withstand heating & Cooling cycles ?
- How does the Molecular Weight Distribution of the material is affected by repeated Heated & Cooling Cycles?
- Polymer Processing Simulating Conditions (Measure Melt Torque,  $f(\text{time})$  with a Lab Mini-extruder).

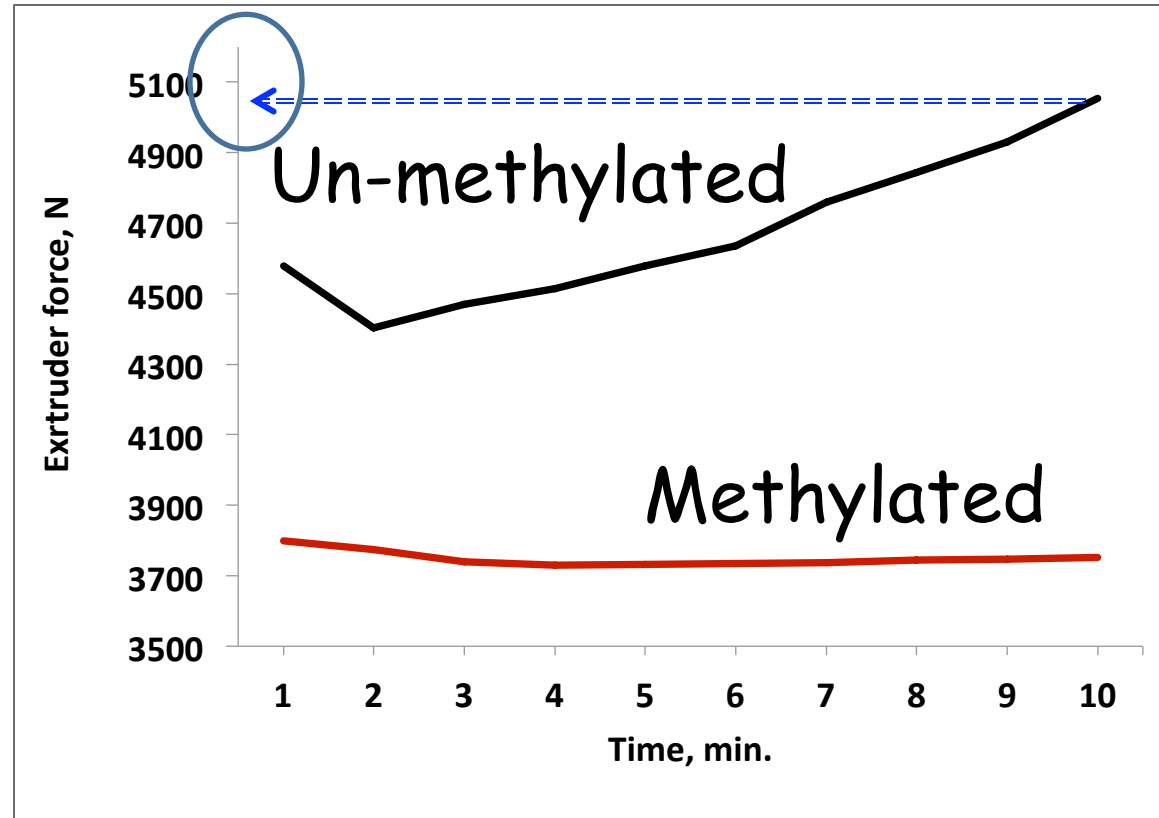
# Minute Changes in the Mol. Wt Distributions are Indicative of the Sought Chemically Stable Melt Characteristics



Cui, C., et al. "Toward Thermoplastic Lignin Polymers; Part II:  
" BioResources 8(1), 864-886, (2013).

# Comparison of Torque ( N ) as a function of melt mixing time for Blends of PP with Non Derivatized (Un-Methylated) and Fully Methylated Kraft Lignin

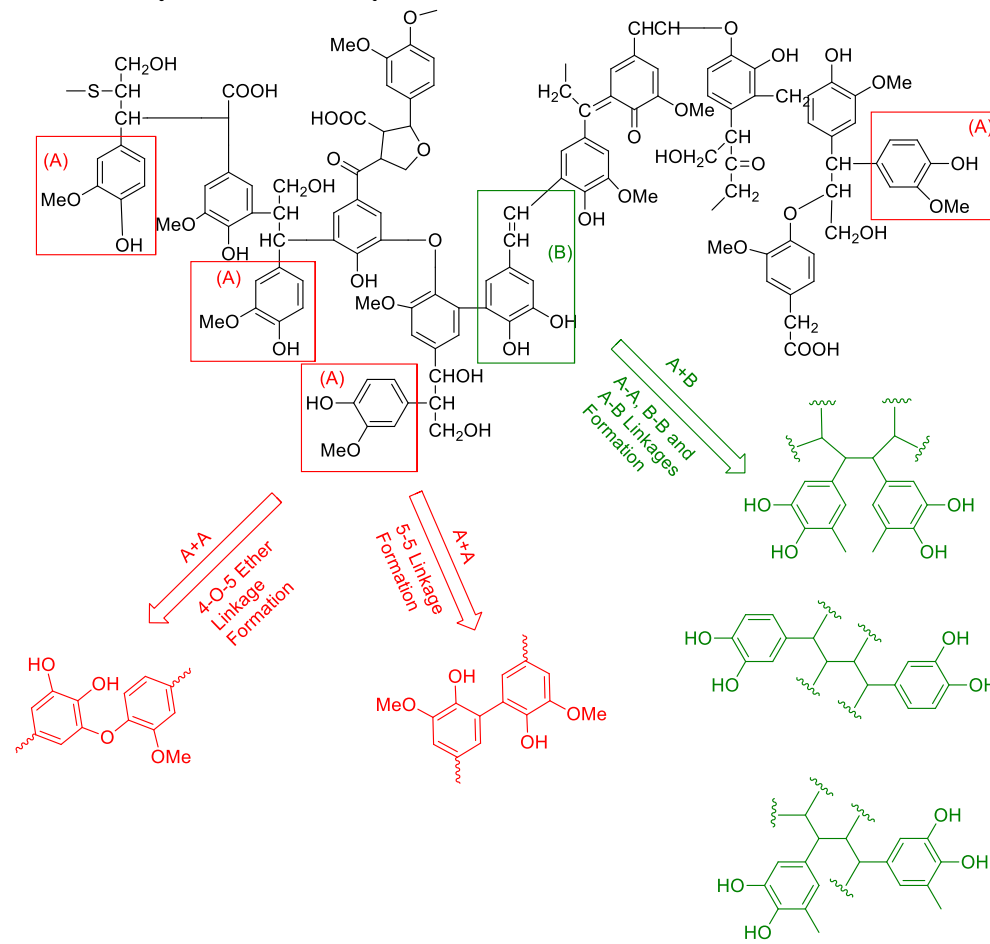
25% lignin



There is no melt stability for non-derivatized Kraft Lignin due to the onset of crosslinking reactions

The melt stability of methylated Kraft Lignin has been verified using melt torque measurements

A multitude of inter & intra molecular thermal events in Kraft lignin may be avoided by the selective and complete methylation of its phenolic OH groups. Thus preventing the phenoxy radicals & QM's from forming and reacting .



# Toward Carbon Fibers from Technical Lignin

Defining the Science & a Novel Approach aimed at  
Creating Carbon Fibers from Lignin Melts

S. Sen, et al. "Toward Thermoplastic Lignin Polymers; Part III:  
" Biomacromolecules (2013).



Since derivatization of the Phenolic OH allowed the modulation of the thermal stability...

Eventual aim: Carbon Fibers from Lignin

- Can one modulate thermal crosslinking?
- Can one regulate the rate of Mol. Weight Increase?
- By introducing activated (thermally labile) centers how does the Molecular Weight Distribution of the material is affected ?

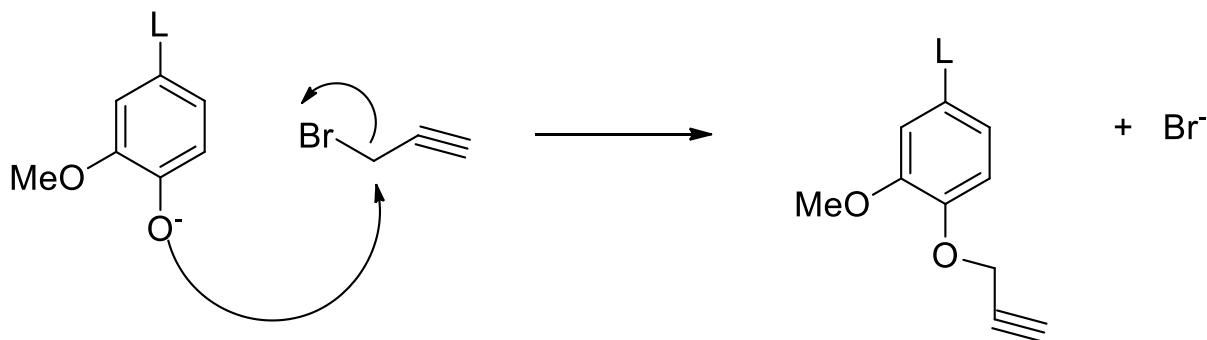
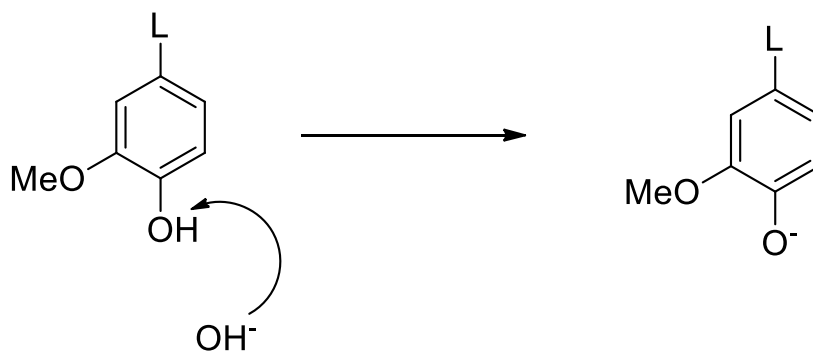
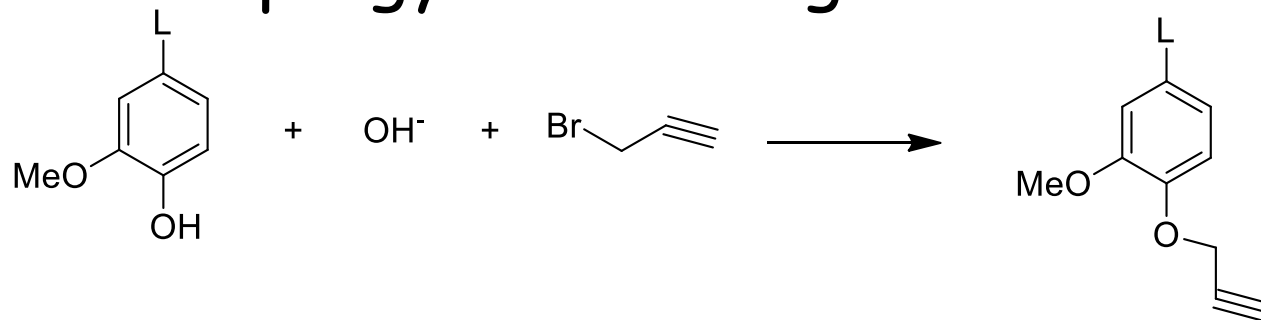


# Towards Reactive Extrusion Lignins

Kraft Lignin Chain Extension Chemistry via  
Propargylation, Oxidative Coupling & Claisen  
Rearrangement

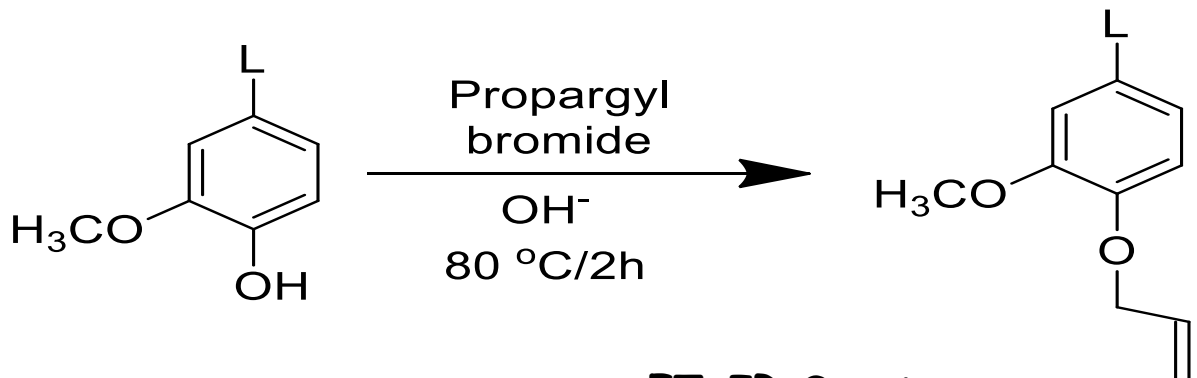
Biomacromolecules : <http://dx.doi.org/10.1021/bm4010172>,

# Propargylation of lignin

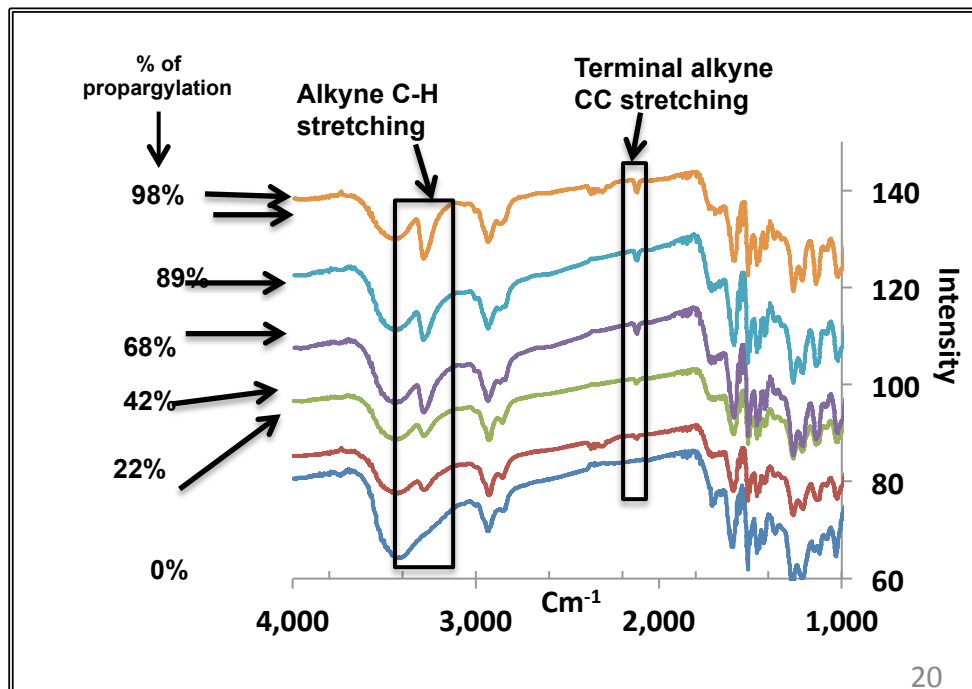




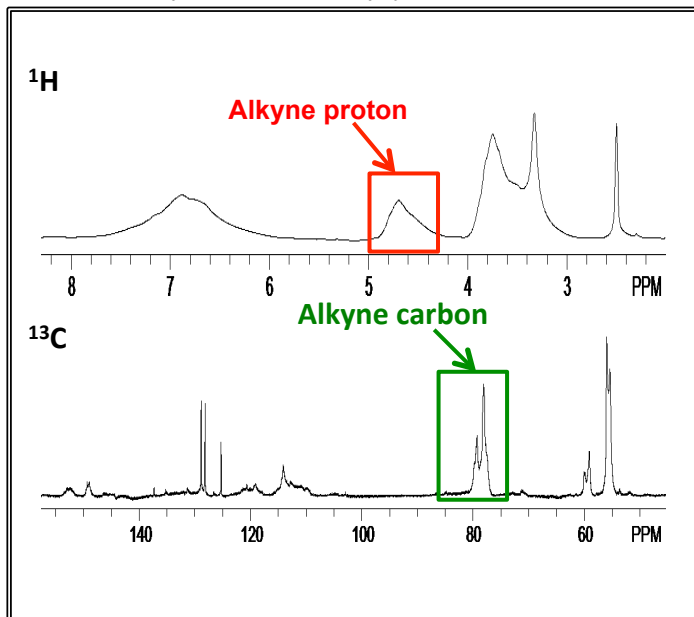
# Initial Characterizations of Propargylated Lignin



## FT-IR Spectroscopy

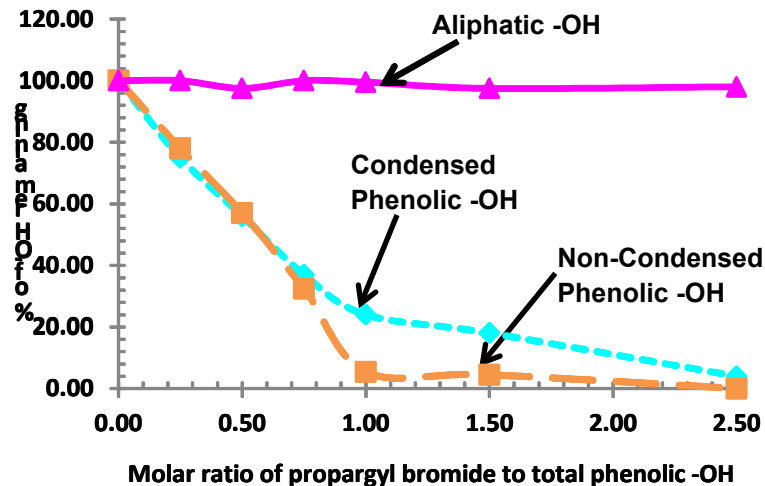


## NMR Spectroscopy





## Reactivity of Lignin Hydroxyl Groups Towards Propargylation



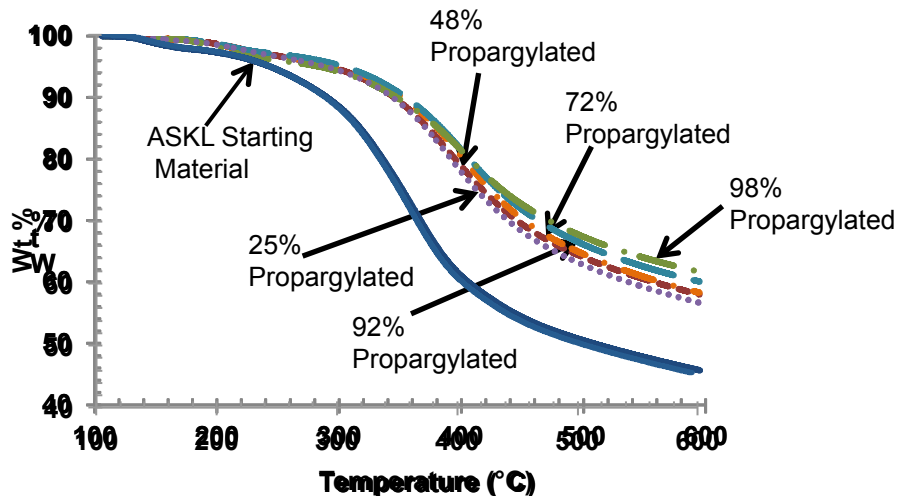
- Initial reaction rate of the condensed phenolic -OHs are same as non-condensed phenolic -OHs
- However the rate of substitution slows down in non-condensed phenolic -OHs in the latter part
- Aliphatic -OHs remain unaffected during propargylation reaction

Biomacromolecules : <http://dx.doi.org/10.1021/bm4010172>,



# Thermal Properties of the Propargylated Lignin

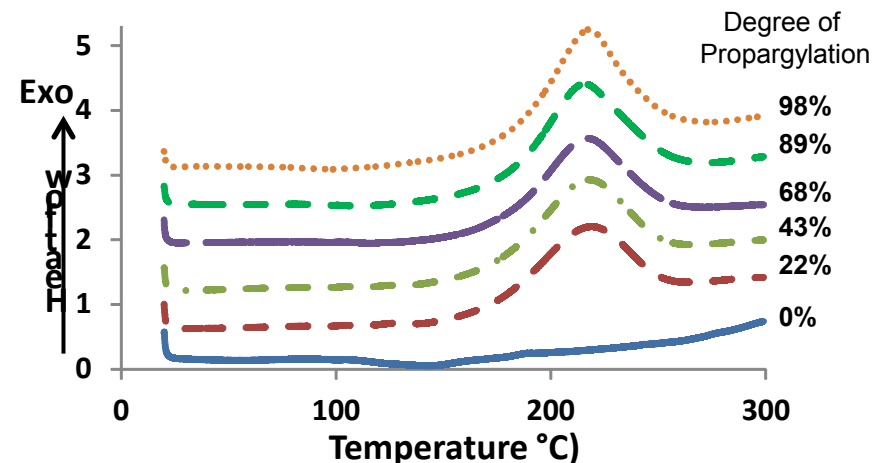
## TGA Traces



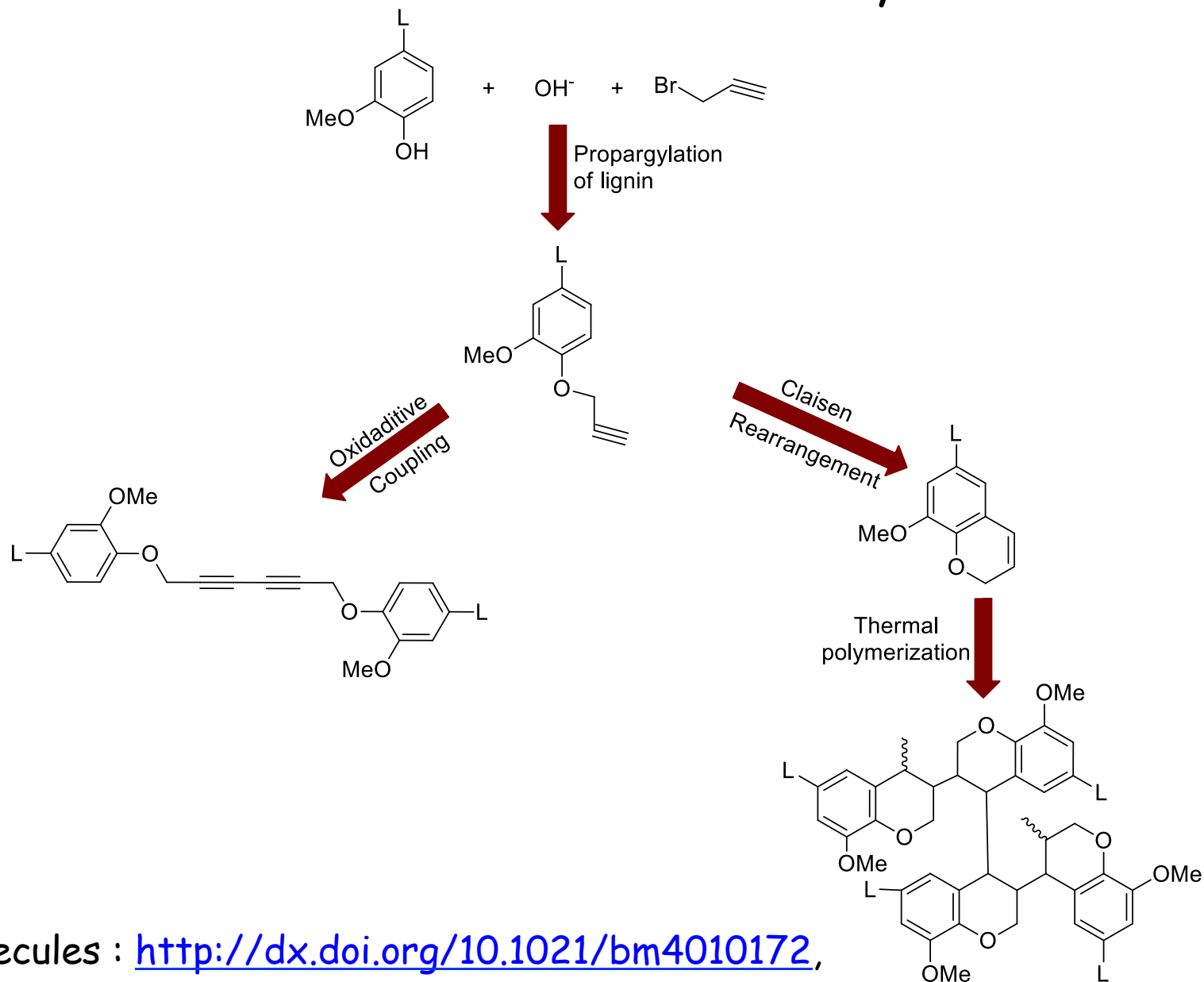
- The thermal stability increases significantly after propargylation
- The thermal stability keeps on improving marginally with the increase of degree of propargylation

## DSC Traces

- DSC traces show an exotherm with an onset and a maximum around 150 °C and 215 °C respectively

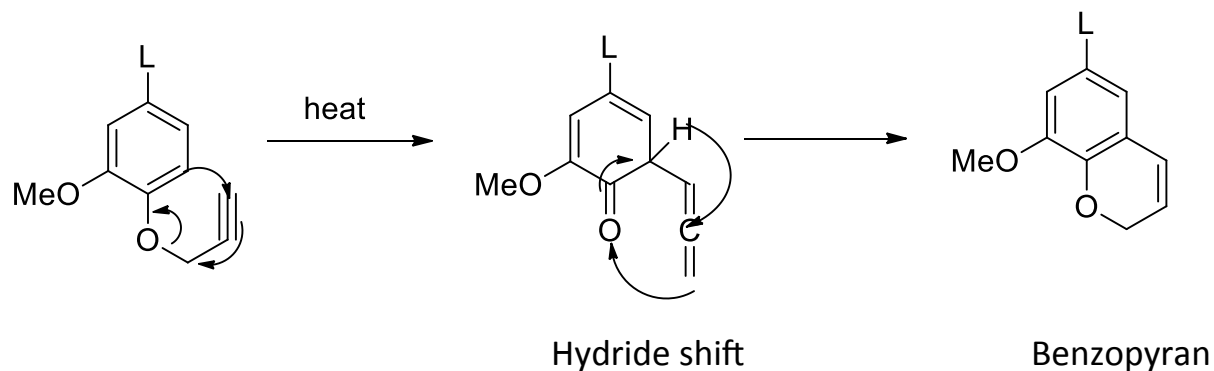


# The Versatility of the Installed Propargyl Groups Toward Chain Extension Chemistry

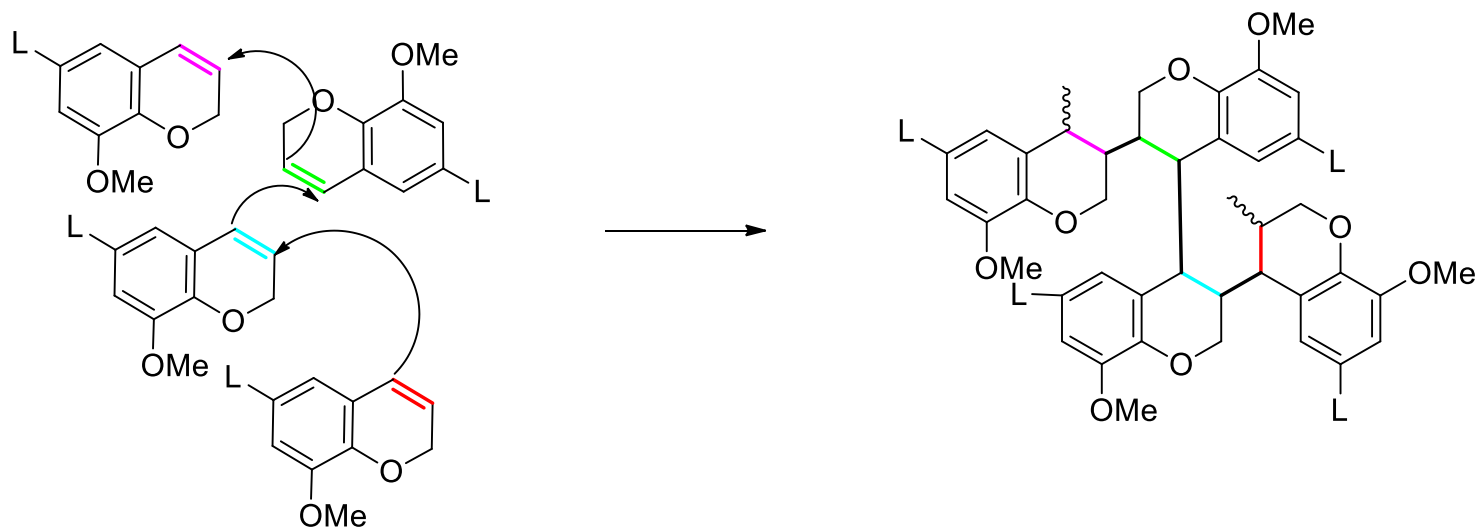


# Thermally Induced Polymerization of the Propargylated Lignin

## Claisen Rearrangement



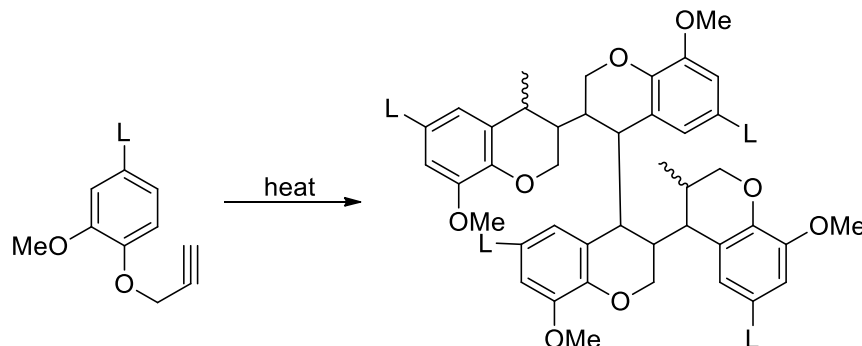
## Thermal Polymerization





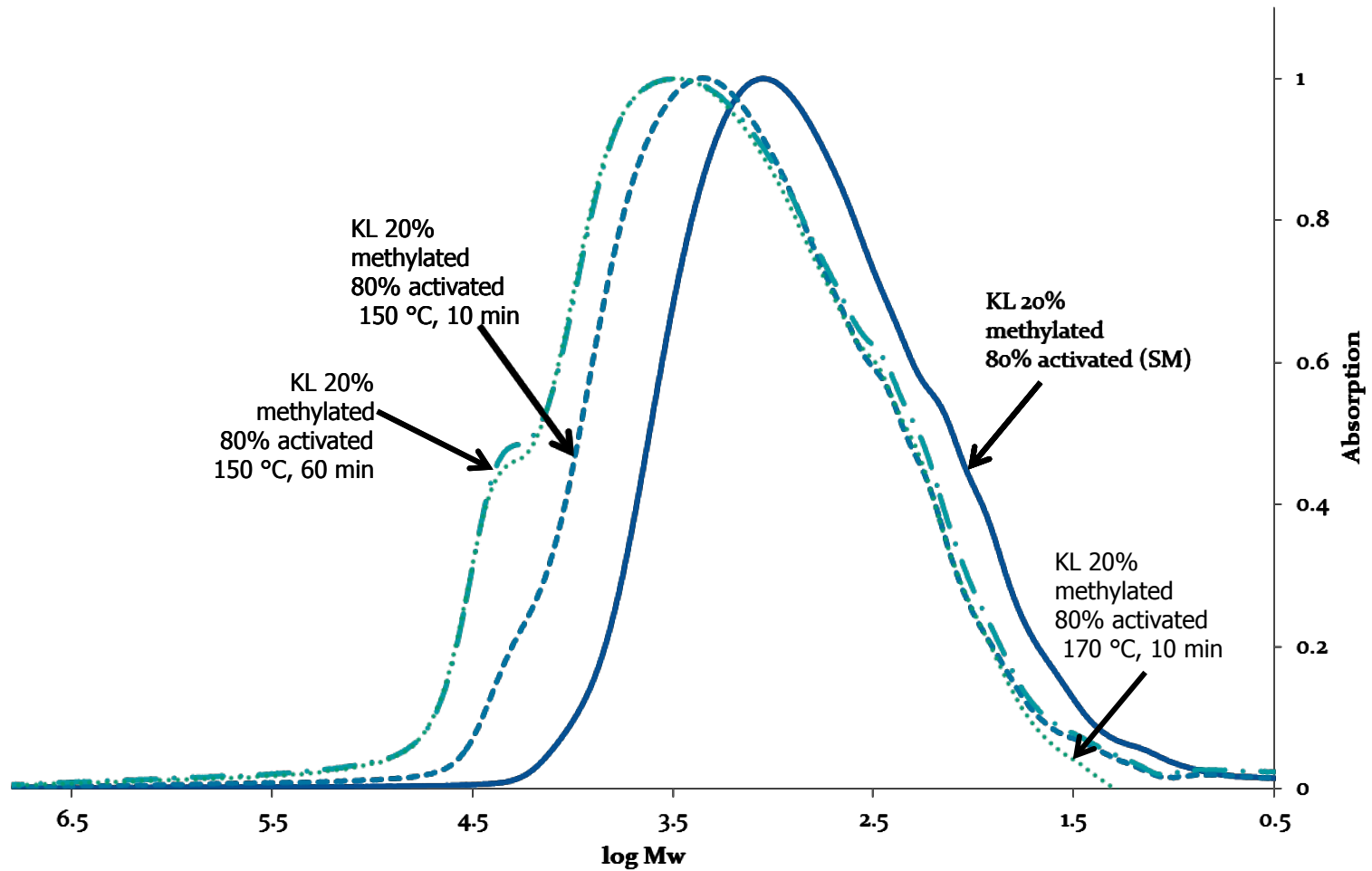


## Bulk Thermal Polymerization of the Propargylated Lignin



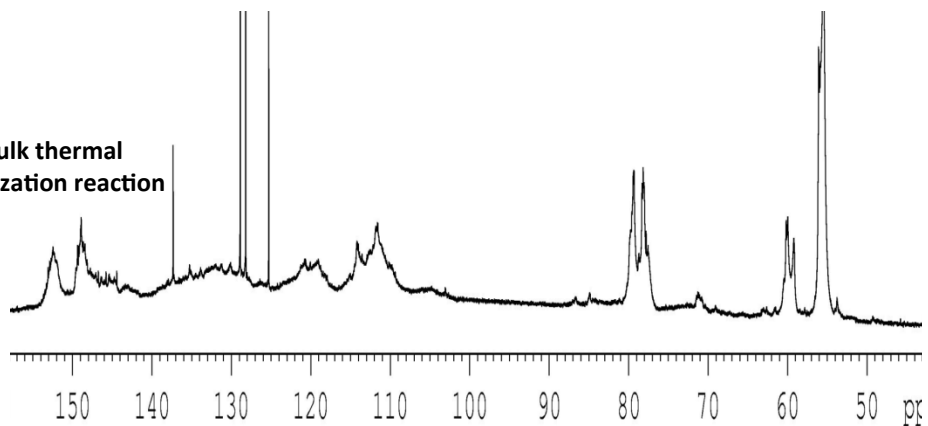
- About 40 mg of the propargylated softwood kraft lignin samples were heated within the chamber of a thermogravimetric analysis apparatus (TGA) for predetermined times at predetermined (to optimize the molecular weight) temperatures under a nitrogen atmosphere

	Temperature (°C)	Time (min)	Mn (g/mol)	Mw (g/mol)	PDI
Before thermal polymerization	0	0	1,500	2,160	1.44
Sample 1	150	10	2,100	5,200	2.53
Sample 2	150	60	2,300	10,400	4.49
Sample 3	170	10	2,330	11,400	4.88
Sample 4	170	20	Gelation		

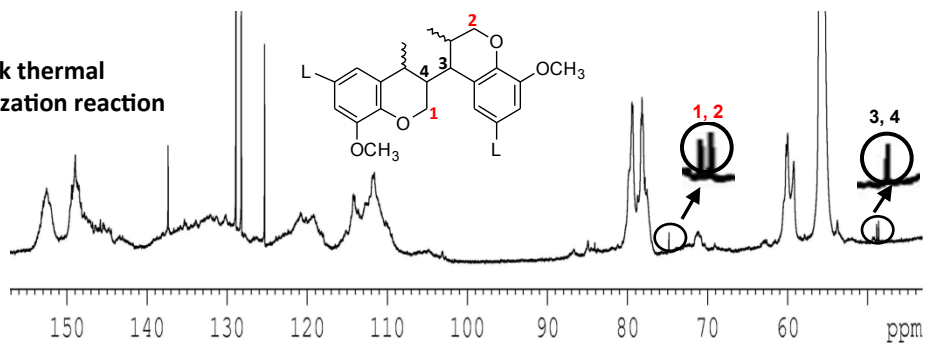


The molecular weight distribution gradually increases with increasing temperature and time of heating

Before bulk thermal  
Polymerization reaction



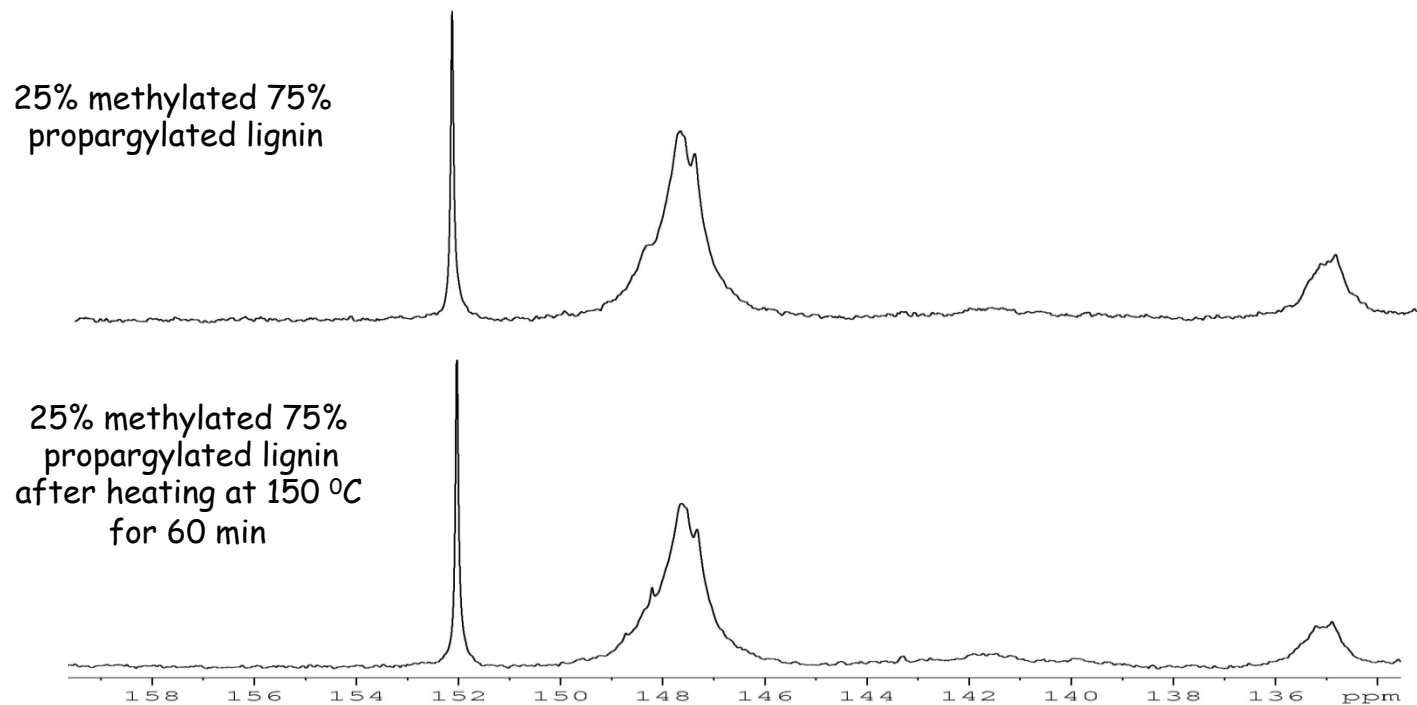
After bulk thermal  
Polymerization reaction



Biomacromolecules : <http://dx.doi.org/10.1021/bm4010172>,



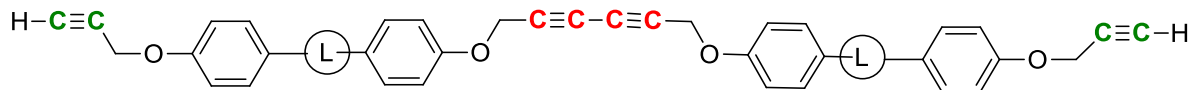
## Stability of Aliphatic and Phenolic -OHs of Lignin after Thermal Polymerization



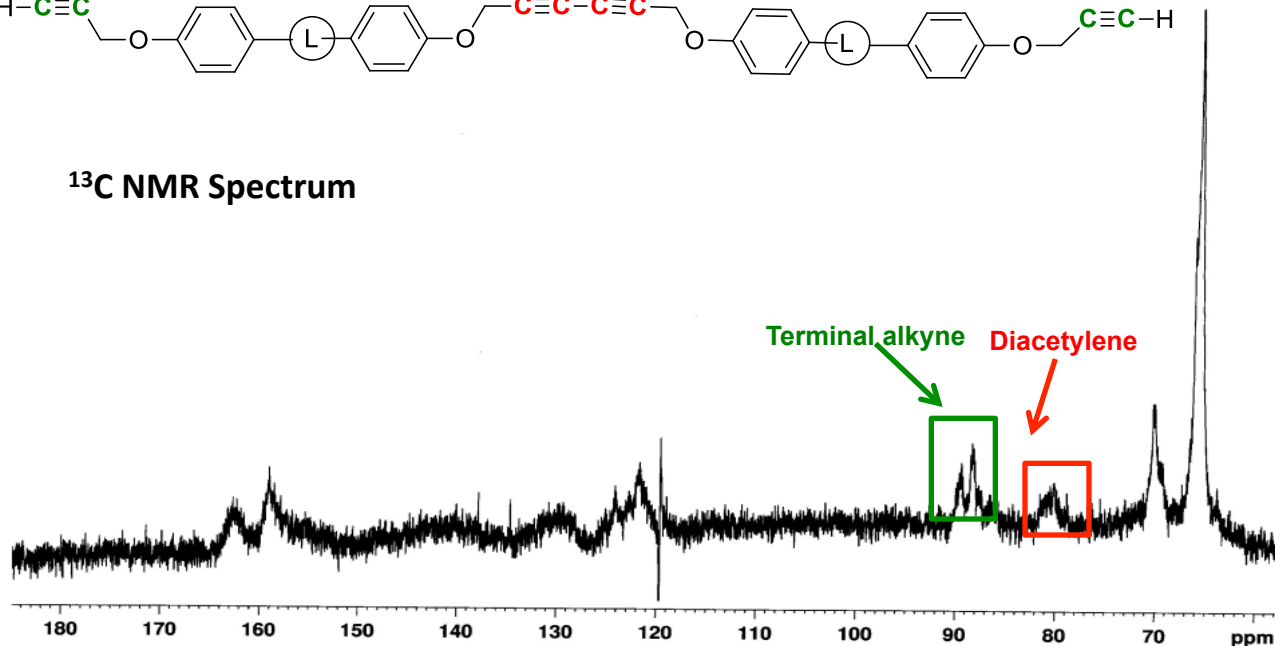
	Aliphatic -OH (mmol/g)	Total phenolic -OH (mmol/g)	Carboxylic -OH (mmol/g)
25% methylated 75% propargylated lignin	1.44	0.36	0.43
25% methylated 75% propargylated lignin after heating at 150 °C for 60 min	1.22	0.40	0.32



## Characterizations of the Coupled Propargylated Lignin



$^{13}\text{C}$  NMR Spectrum



- $^{13}\text{C}$  NMR spectrum of the polymer after the oxidative coupling reaction. The peaks of dialkyne carbons can be clearly seen between 68 to 72 ppm.
- Peaks between 85 to 91 ppm are due to unreacted terminal alkynes



## Oxidative Coupling of the Propargylated Lignin

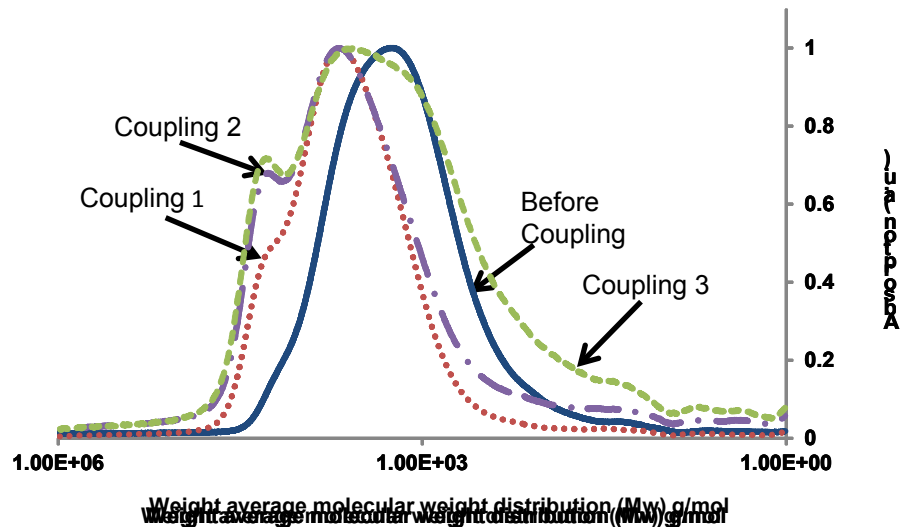
Oxidative coupling reaction was conducted at different temperature and for different time period (as shown in the following table) to optimize the molecular weight distribution

	Lignin sample used for coupling reaction	Temperature (°C)	Time (h)	Mn g/mol	Mw g/mol	PDI
Coupling 0	98% propargylated	25	1			Gelation
Before coupling	25% methylation 75% propargylation	0	0	1,500	2,140	1.42
Coupling 1	25% methylation 75% propargylation	25	24	2,100	3,600	1.71
Coupling 2	25% methylation 75% propargylation	60	24	2,300	10,000	4.68
Coupling 3	25% methylation 75% propargylation	80	6	2,000	11,000	5.77
Coupling 4	25% methylation 75% propargylation	80	24			Gelation

Biomacromolecules : <http://dx.doi.org/10.1021/bm4010172>,



# Molecular Weight Distributions

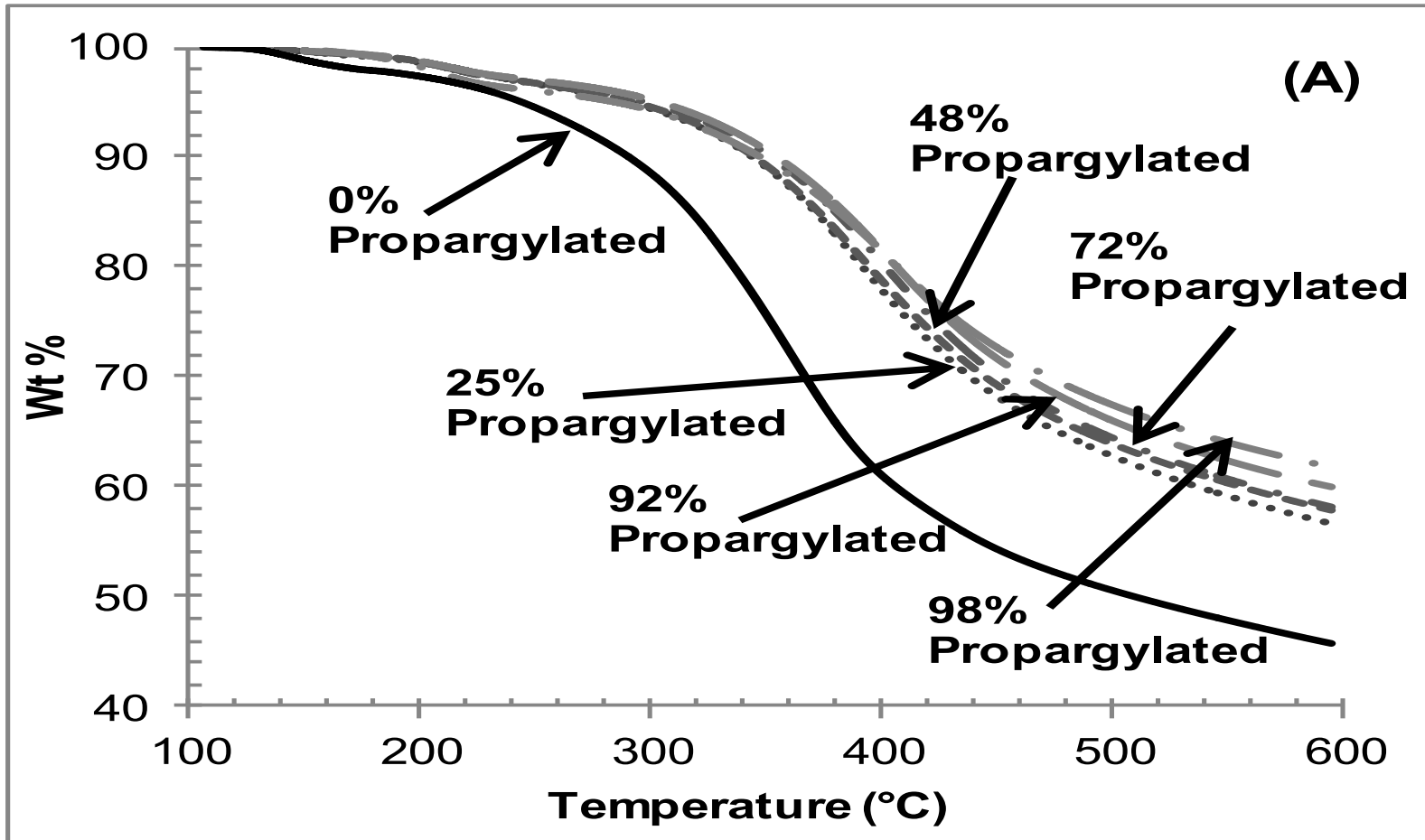


- With the increase in time and temperature of the reaction medium the molecular weight distribution curves shift towards the higher molecular weight direction showing progression in the polymerization reaction

Biomacromolecules : <http://dx.doi.org/10.1021/bm4010172>,



## Thermal Properties after Oxidative Coupling Reaction



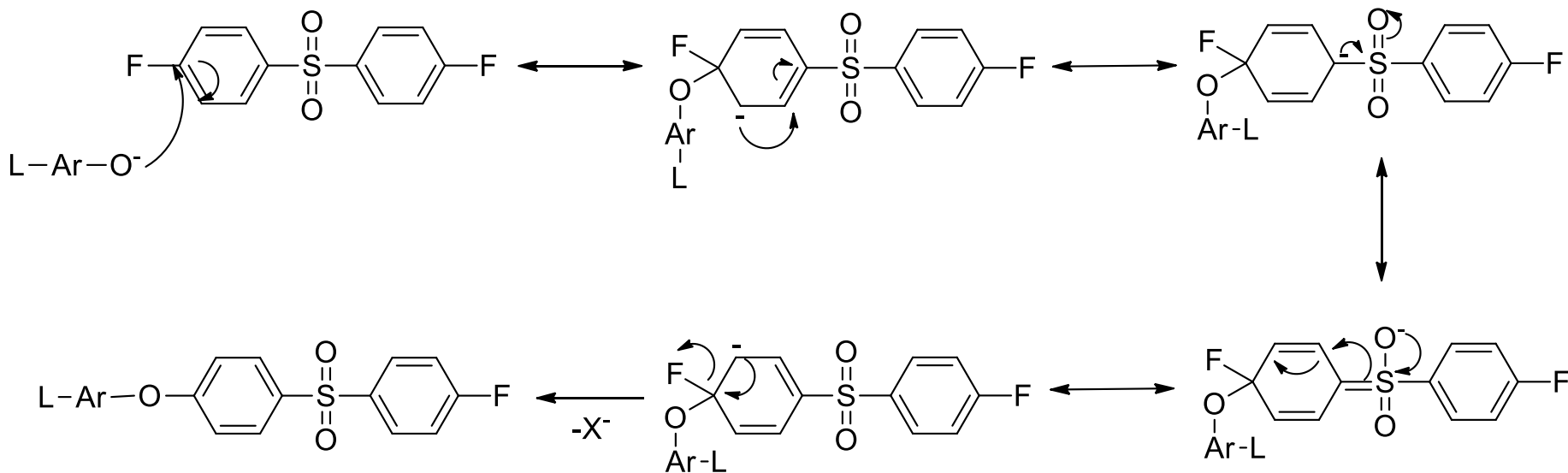
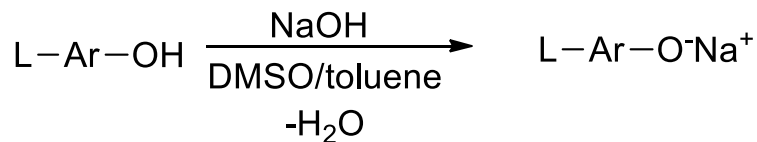


# Toward Heat Stable Poly (Arylene Ether) Sulfone-Lignin Heat Stable Copolymers

## Why Poly (Arylene Ether Sulfones)

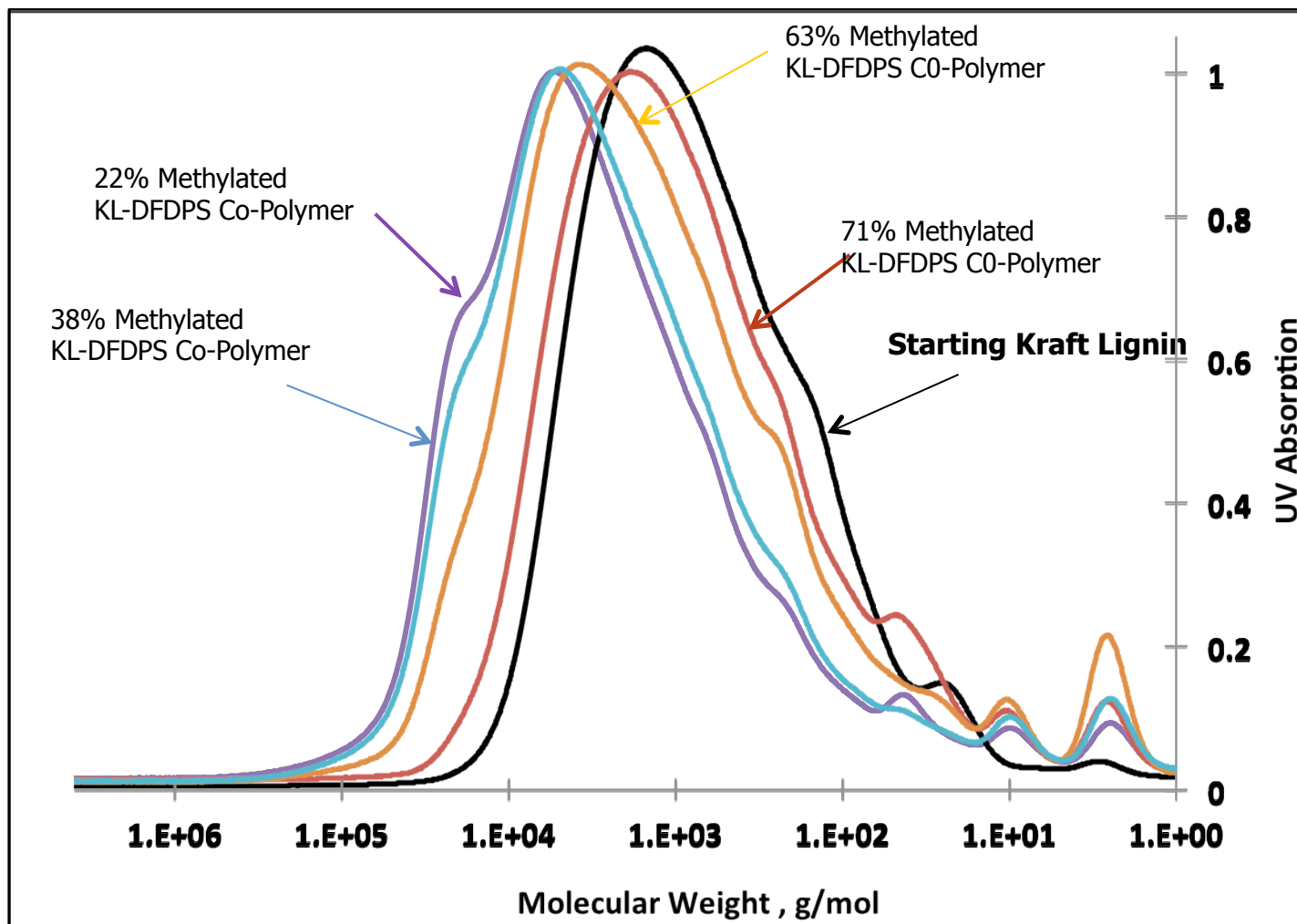
- Ease of preparation,
- Ease of functionalization,
- Thermal & chemical stability
- Relatively low cost
- Excellent mechanical performance.

# Copolymerization of Kraft Lignin with Difluorodiphenyl Sulfone (DFDPS)



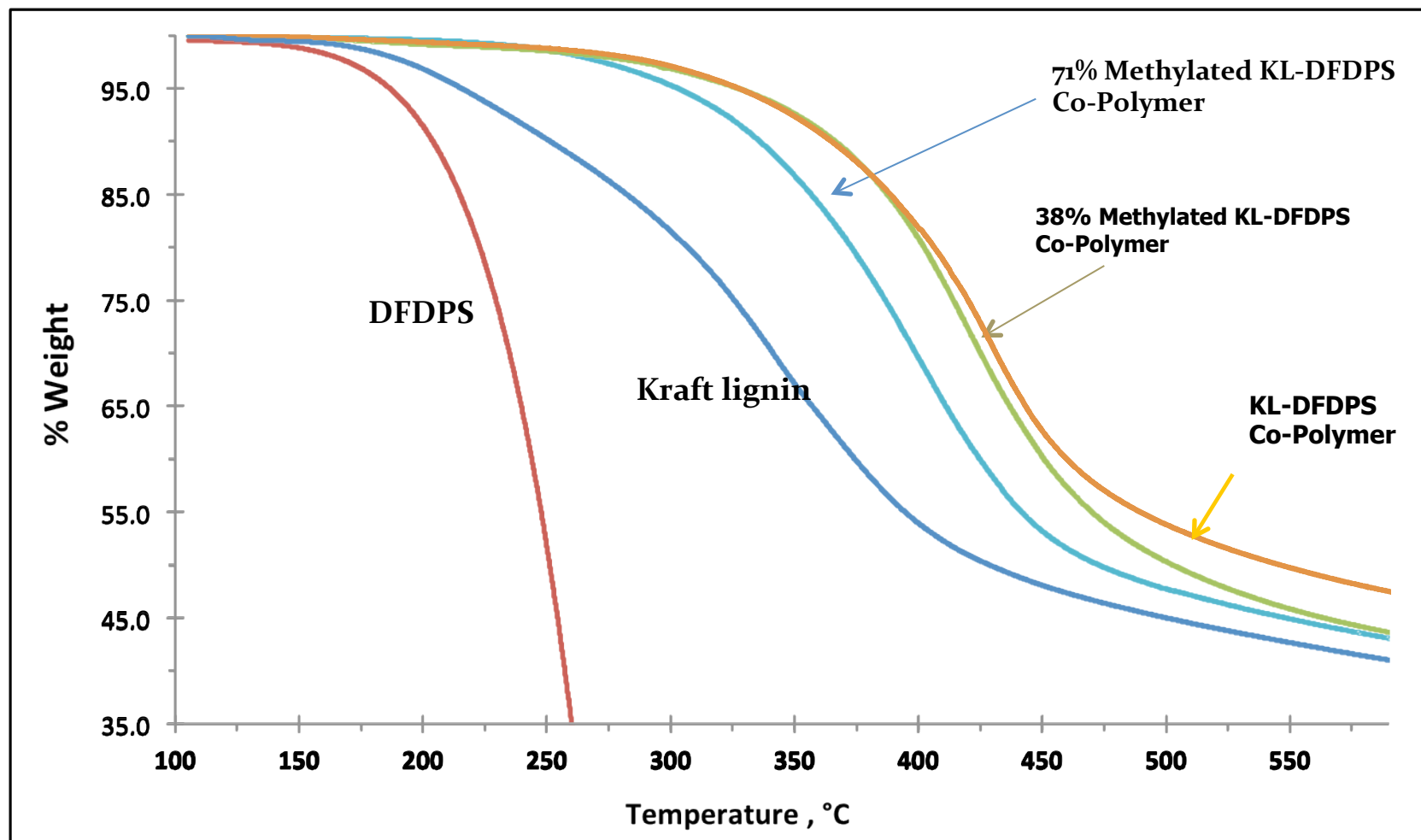
$\text{L-Ar-OH}$  = Lignin molecule with phenolic -OH end group

# Size Exclusion Chromatographic Analyses of Methylated Kraft Lignin DFDPs Co-Polymers .



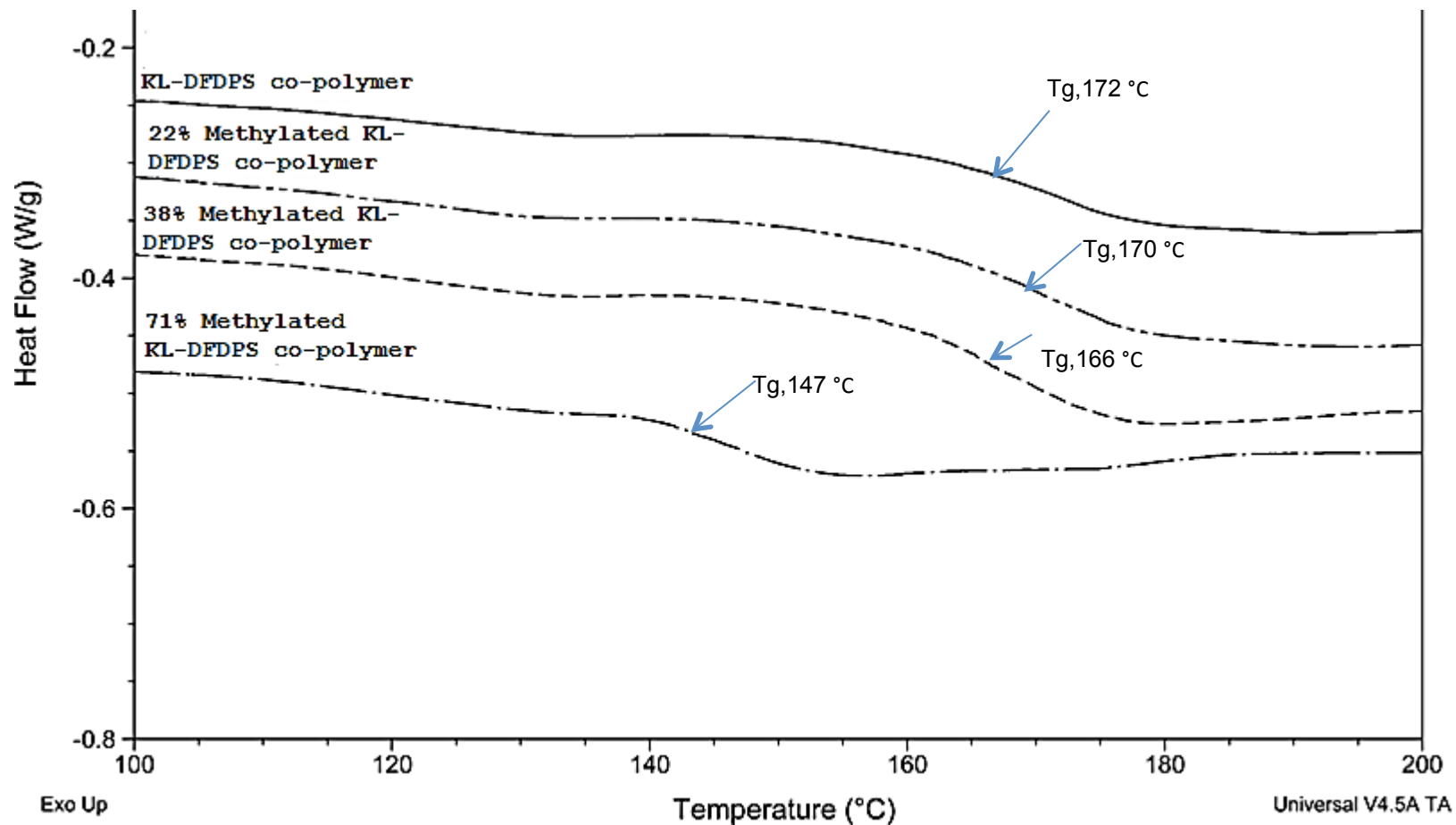
Typical Step growth polymerization Mol wt. distribution shapes are observed, progressively moving to higher molecular weights

# Thermal Degradation Analyses of Methylated Kraft Lignin DFDPS Co-Polymers

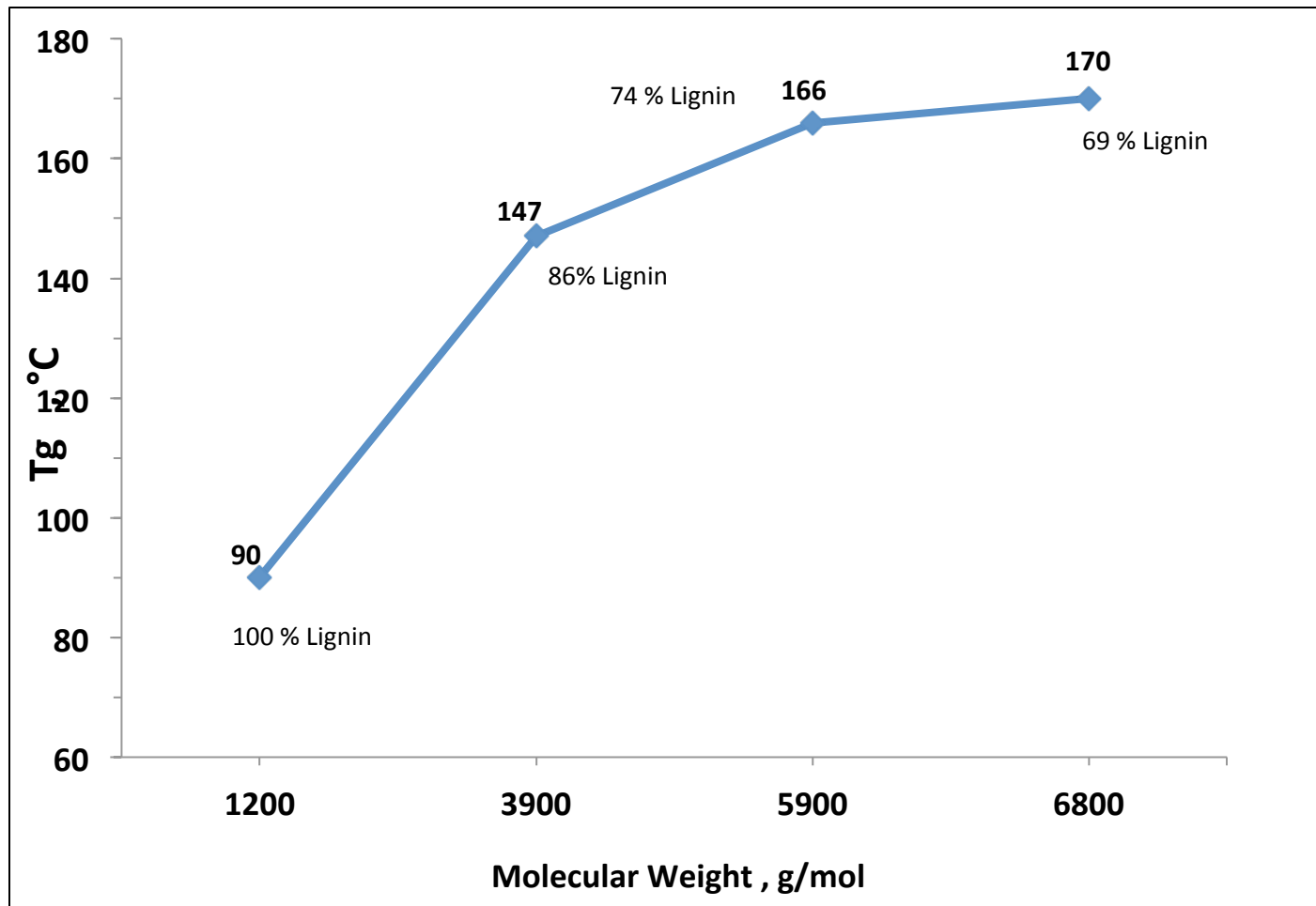


Heat stabilities up to 270 °C are observed for these Kraft Lignin DFDPS Copolymers with T<sub>g</sub> values at least 100 °C lower

# Differential Thermal Scans of Methylated Kraft Lignin DFDPS Co-Polymers .



# Glass Transitions Temperature ( $T_g$ ) as Function of Molecular Weight for a Series of Kraft Lignin -DFDPS Co-Polymers



## Conclusions

- The selective methylation of the phenolic OH is pivotal in controlling the thermal stability of technical Lignin
- Molecular Weight Distribution & Melt Extrusion Torque measurements offer a detailed way of understanding such thermal events
- Lignin propargylation/methylation offers a versatile new avenue towards lignin chain extension, reactive extruding and carbon fiber precursors.

## Conclusions

- Thermoplastic Co-polymers of Polyarylene ether Sulfones with Kraft Lignin have been synthesized displaying :
  - Typical Step Growth Mol. Weight Distributions
  - Excellent Thermal Stability
  - Predictable Mol. vs Wt. Tg Relations



# Strategic Decisions

- Treating Lignin with respect will pay off
- Focus & capitalize on current limitations
- Expand into Hardwood & Biorefinery Lignins
- Work with Specific Lignin for specific high value applications
- Work with Industry to bring these to further development

# Acknowledgments

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