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Developing A New Polyolefin Precursor for Low-Cost, High-Strength Carbon Fiber

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DOE Hydrogen Program Annual Merit Review and Peer Evaluation Meeting
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Project ID: ST147

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Project start date: 9/1/2017
- Project end date: 8/31/2020
- % complete: 30%

Budget

- Total project funding: $930,888

- DOE share: $804,462
- Penn State share: $127,181

- Funding for FY2017-18: $ 306,363
- Go/no-Go decision: August 2018

Barriers

- System weight & volume
- System cost, efficiency, durability
- Charging/discharging rates
- Suitable H_2 binding energy
- High polymer surface area

Partners

- LightMat consortium
- Oak Ridge National Lab.

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Relevance

Research Objectives

- Developing a new polyolefin precursor that is melt-processible and high thermal conversion yield to form carbon fiber (CF).
- Co-carbonization with B-containing precursor to prepare B-doped CF with reduced temperature, high yield, smaller d-spacing.
- Cost savings can be realized through the combination of low cost precursor, melt-spinning fiber process, low carbonization temperature, high mass yield, and high tensile strength in the B-doped CF.

Potential Benefits and the Impact on Technology

- If successful, this new technology can offer a cost-effective CF for fabricating onboard storage vessel with compressed hydrogen (700 bars) in FCEVs. The main objective is to achieve the DOE cost target of \$10/kWh (about \$1,900 per vehicle with 5.6 Kg of usable hydrogen). It also can impact other energy-relative applications, such as wind blades, flywheels, transportation, etc.

Relevance: DOE cost targets

5 gallon tank with 700 bars pressure
5 kg H_2 storage for 300 miles driving range (45-60 miles/kg H_2)
High Cost (~ $3,000 per vehicle)

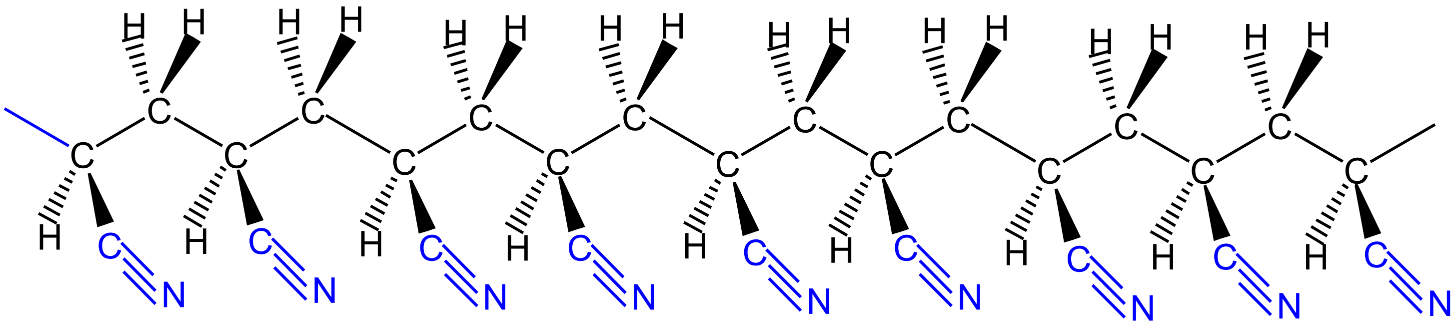
Composite overwrapped pressure vessel for 5.6 Kg usable hydrogen		
	Energy cost ($/kWh)	System cost ($/vehicle)
2013 system	$17	$3,200
2015 system	$15	$2,800
DOE Target	$10	$1,900

Type IV COPV system with polymer liner and annual production rate of 500,000 systems

DOE 2015 cost analysis indicated that 62% of the system cost would come from the cost of carbon fiber (CF)

Relevance: Current CF precursors

Polyacrylonitrile (PAN)

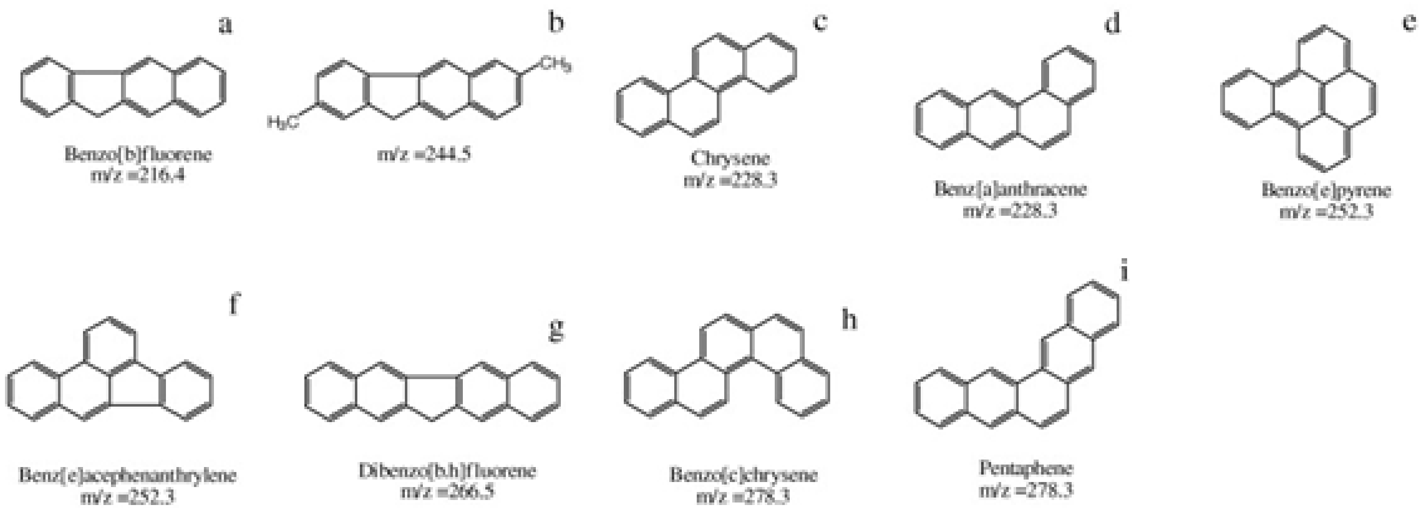


Pitch (petroleum)

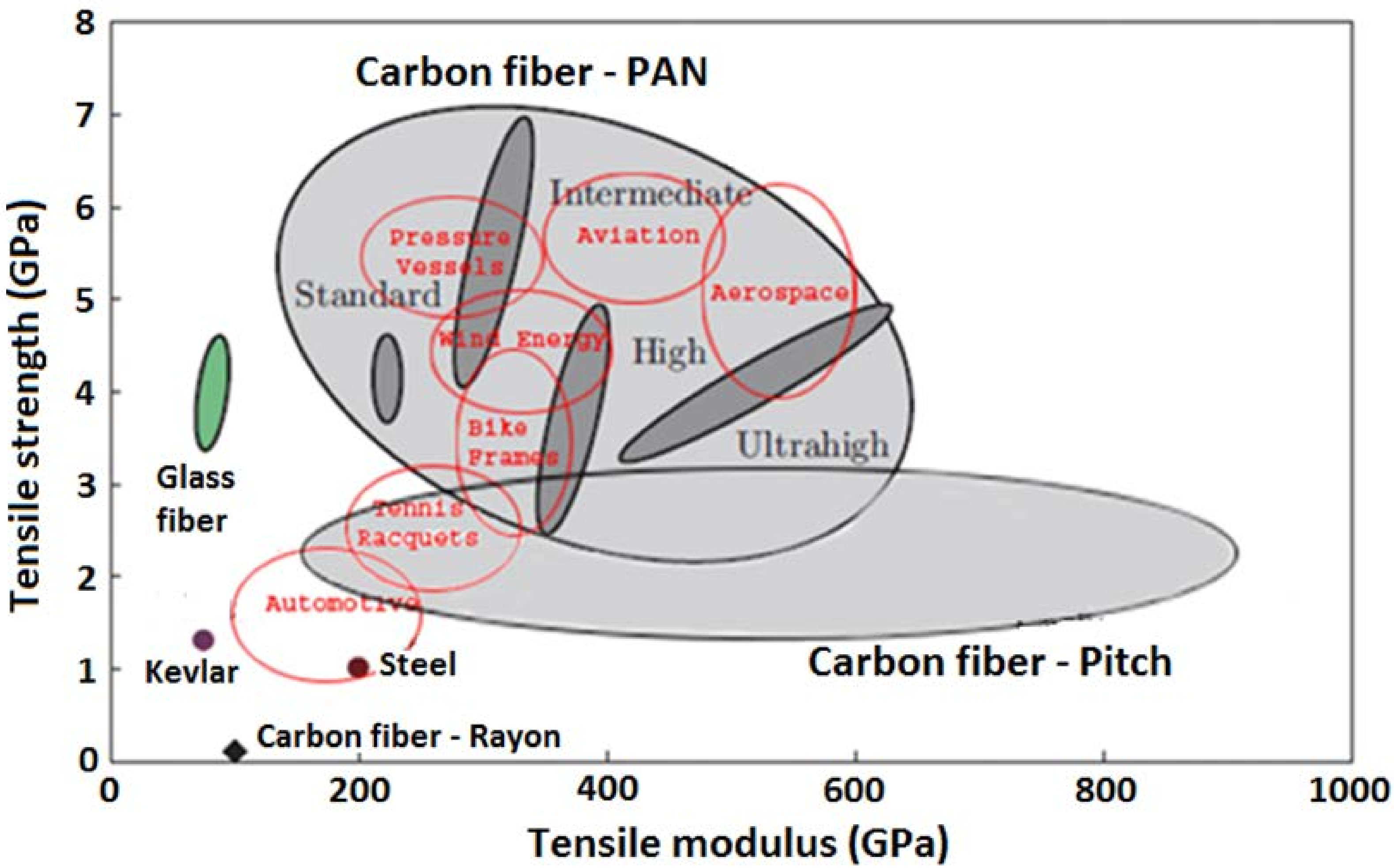
Oligomeric mixture of polycyclic aromatic hydrocarbons (PAH) with molecular weight 200-800

Pitch (coal tar)

PAH and Phenols make up two large classes of chemicals.



Relevance: Tensile Properties



Advantages of Pitch precursor:
Low cost, melt-processible, and high C yield (up to 70%)

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Relevance: Current thermal production process

PAN Polymer Precursor → wet spinning + stretching → **PAN Fiber**

PAN Fiber → ▲ air → **Stabilization** (200-300 °C in air for 30-120 minutes) + Stretching

Stabilization → ▲ N_2 → **Carbonization** (1000-2000 °C in N_2 atmosphere) + Stretching

Carbonization → **Surface Treatment & Sizing**

PAN fiber going through oxidation oven

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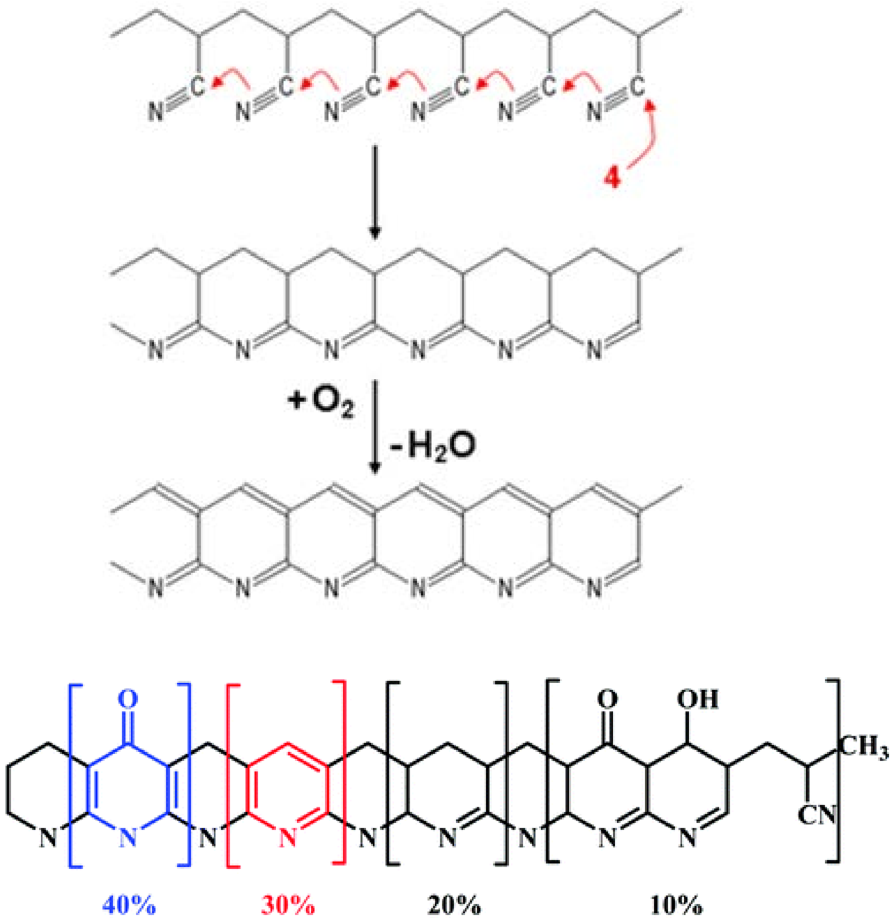
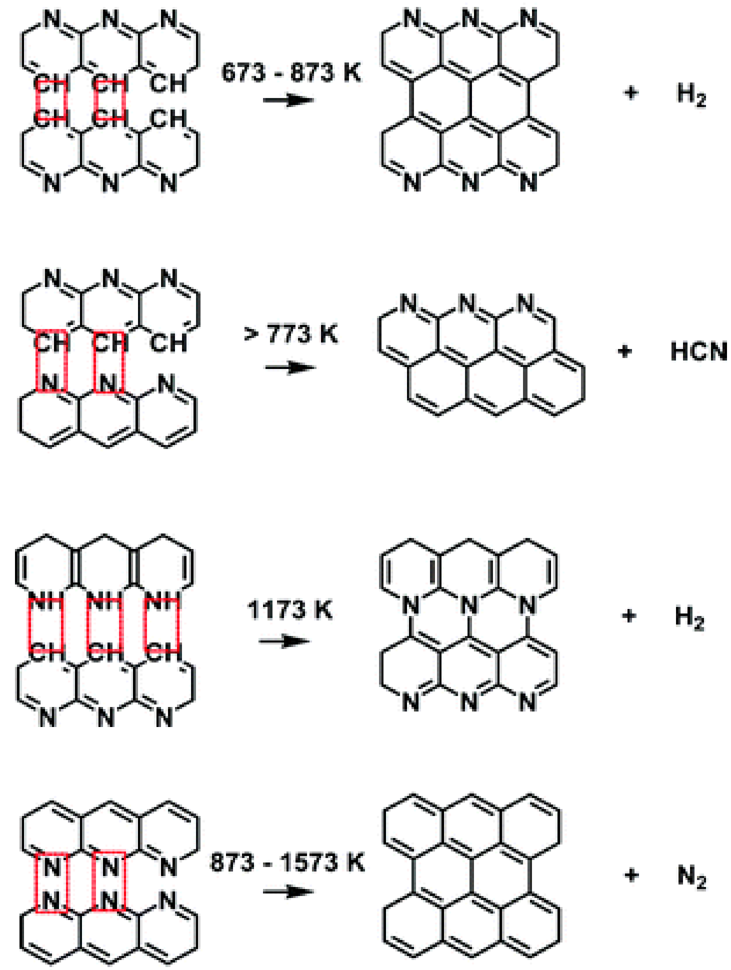
Relevance: PAN thermal conversion

Stabilization
(200-300 ^{o}C)



Carbonization
(1000-2000 ^{o}C)



Overall thermal conversion yield ~50%

Milestone Summary Table							
	Recipient Name:	T. C. Mike Chung					
	Project Title:	Developing A New Polyolefin Precursor for Low-Cost, High-Strength Carbon Fiber					
Task Number	**Task or Subtask (if applicable) Title**	**Milestone, Go/No-Go Decision**	**Milestone Number**	**Milestone Description (Go/No-Go Decision Criteria)**	**Milestone Verification Process***	**Anticipated Date (Months)**	**Anticipated Quarter (Quarters)**
1	**Synthesis of Diene Monomers**	Milestone	M1.0	Synthesis route and two diene monomers	^{1}H and ^{13}C NMR spectra of the resulting monomers.	1-2	1
2.1	**Synthesis of PE Copolymers with DVB and BSt units**	Milestone	M2.1	Confirm two resulting polymer structures	GPC curves and ^{1}H NMR spectra of two polymers.	3-6	1-2
2.2	**Synthesis of Poly(DVB) and Poly(BSt) Homopolymers**	Milestone	M2.2	Confirm two resulting polymer structures	GPC curves and ^{1}H NMR spectra of two polymers.	7-9	2-3
3	**Stabilization and Carbonization Study**	Milestone	M3.0	Convert precursors to C materials	mass yield, TEM, XRD, elemental analysis.	8-12	2-4
1st Go/No-Go Decision		**A new low-cost polyolefin precursor that can be prepared and transformed to C with mass yield (>80%), more than 60% higher than that of current PAN.**				**Send 10 slides to LightMat /DOE**	
4	**Scaling Up the Selected Polyolefin Precursors**	Milestone	M4.0	Selected precursors with Kg quantity	^{1}H NMR, GPC, DSC and TGA spectra.	13-15	5
5.1	**Melt-Spinning of Polyolefin Precursors**	Milestone	M5.1	Fiber-spinning to polyolefin fibers	Pictures and Strain-stress curves.	16-21	6-7
5.2	**Carbonization of Polyolefin Fibers**	Milestone	M5.2	New polyolefin based CF products	TEM, SEM, XRD, Instron, and elemental analysis .	19-24	7-8
2nd Go/No-Go Decision		**A new low-cost and high-quality carbon fiber obtained from a new polyolefin precursor and melt-spinning process.**				**Send 10 slides to LightMat /DOE**	
6.1	**Co-carbonization study of Polyolefin Blends with B-Precursors**	Milestone	M6.1	New B-doped C (BCx) materials	^{13}C and ^{11}B NMR spectra and elemental analysis	25-30	9-10
6.2	**Melt-Spinning of Polyolefin Blends with B-Precursors**	Milestone	M6.2	Fibers from B-containing polymer blends	Pictures and Strain-stress curves.	28-33	10-11
6.3	**Carbonization of Polyolefin Blend Fibers**	Milestone	M6.3	New B-doped CF (B-CF)	TEM, SEM, XRD, Instron, and elemental analysis	31-36	10-12

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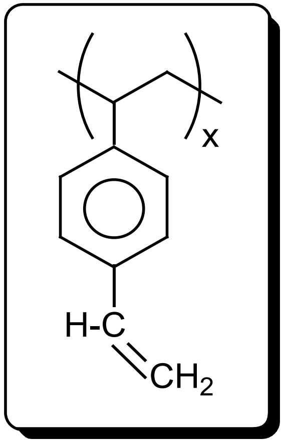
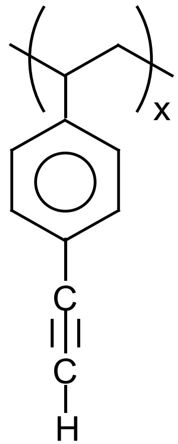
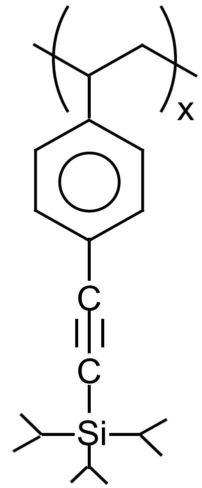
Approach: Design new polyolefin precursors

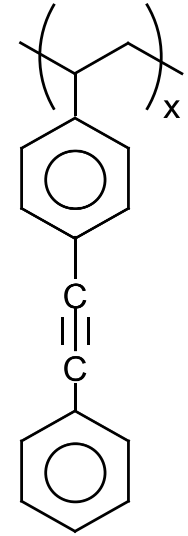
- **Semi-crystalline hydrocarbon polymer (>80% C content)**
- **Melt-spinning to fibers with good tensile strength**
- **Reactive side groups for thermal conversion**
- **Facile stabilization reaction at <300 ^oC**
  - ➢ **Forming <u>ladder/conjugated chain structure</u>**
  - ➢ **No external reagent required**
  - ➢ **No by-product formed, except H_2 and H_2O**
- **Effective thermal conversion with a high C yield (>80%)**
- **Low cost and scalable**

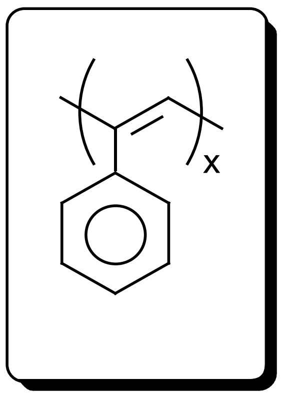
Approach: New polyolefin precursors

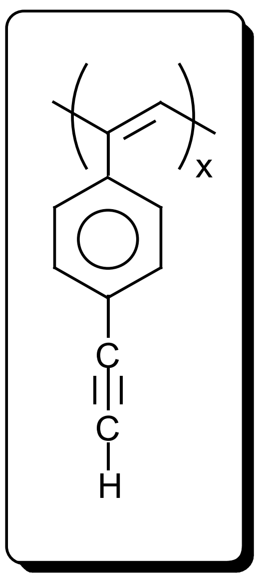


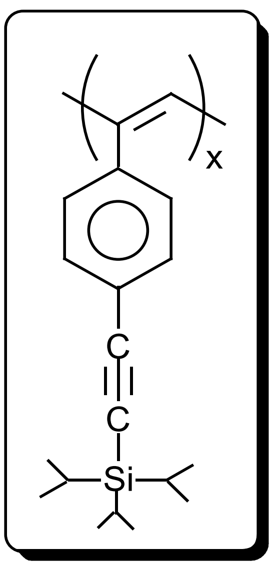


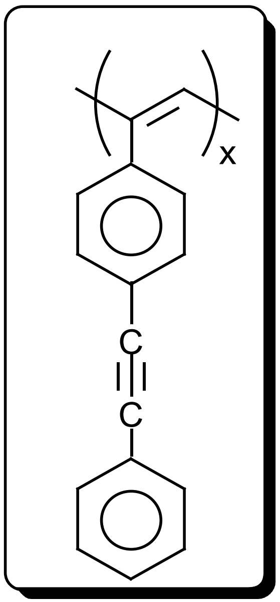












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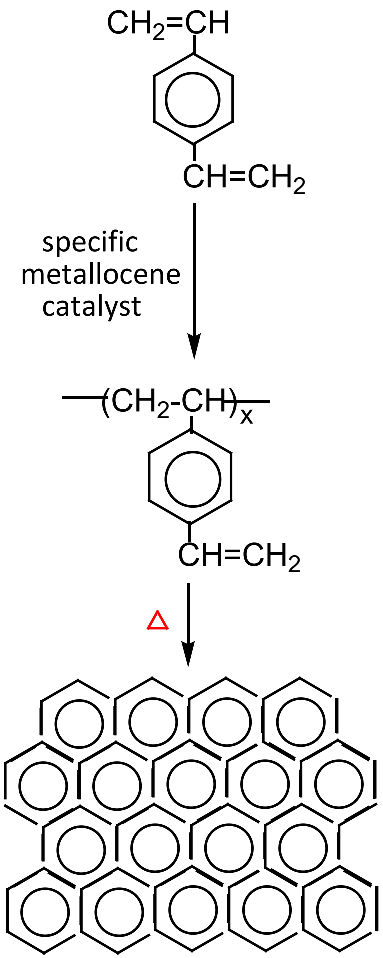
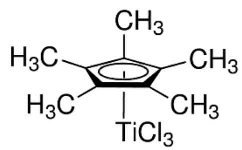
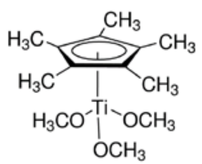
Accomplishments: Synthesis of Poly(divinylbenzene) PDVB precursor





Cp*TiCl$_3$



Cp*Ti(OCH$_3$)$_3$

	Reaction Condition			Polymer product	
	Catalyst	Temp (ºC)	Time (h)	Yield (%)	Product
PDVB-1	Cp*TiCl$_3$	50	3h	48	Gel
PDVB-2	Cp*Ti(OCH$_3$)$_3$	25	12h	90	Soluble

Benefits of Cp*Ti(OCH$_3$)$_3$-mediated polymerization:

- **Mono-enchainment of DVB monomers**
- **Processible PDVB polymer (soluble in solvents)**
- **High polymer conversion**
- **Syndiotactic polymer backbone structure**
- **Semi-crystalline morphology**

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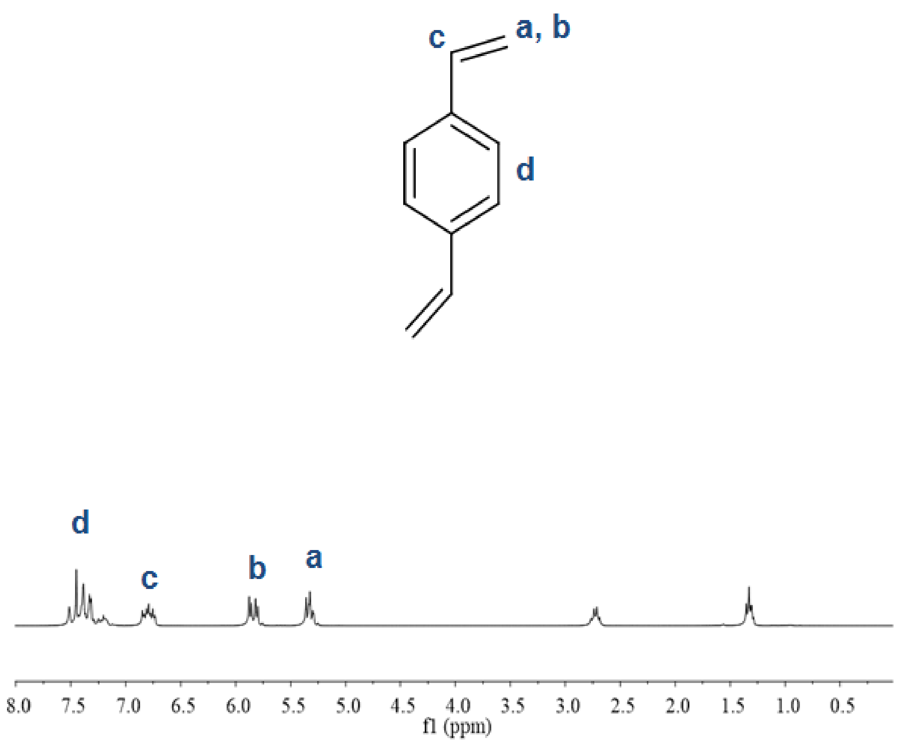
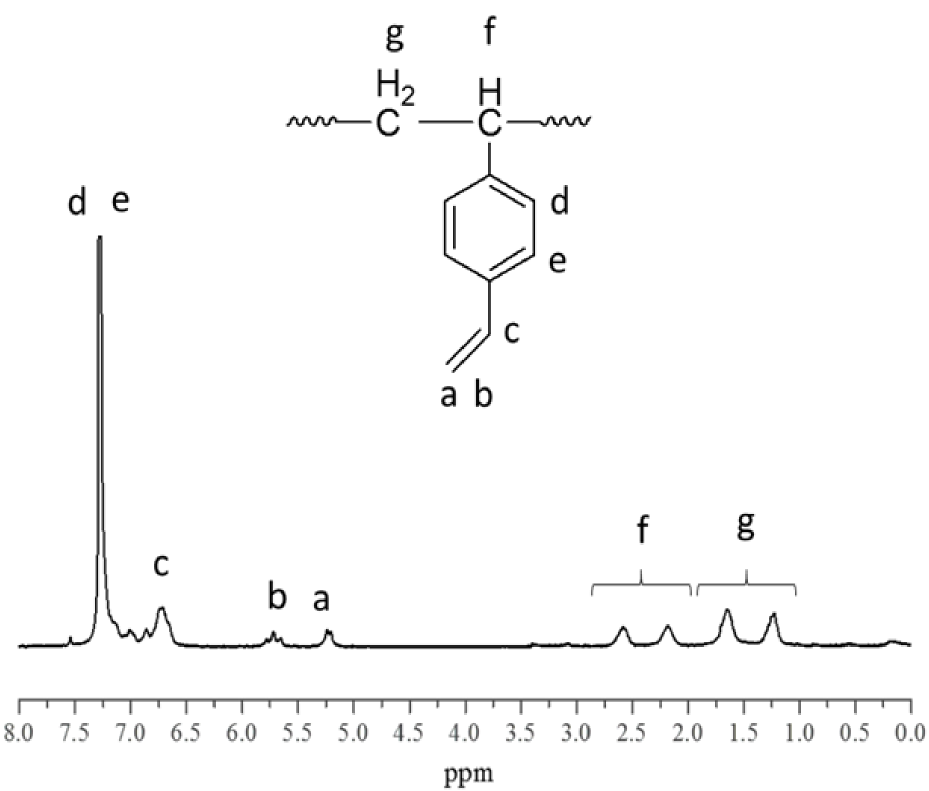
Accomplishments: ¹H NMR spectra

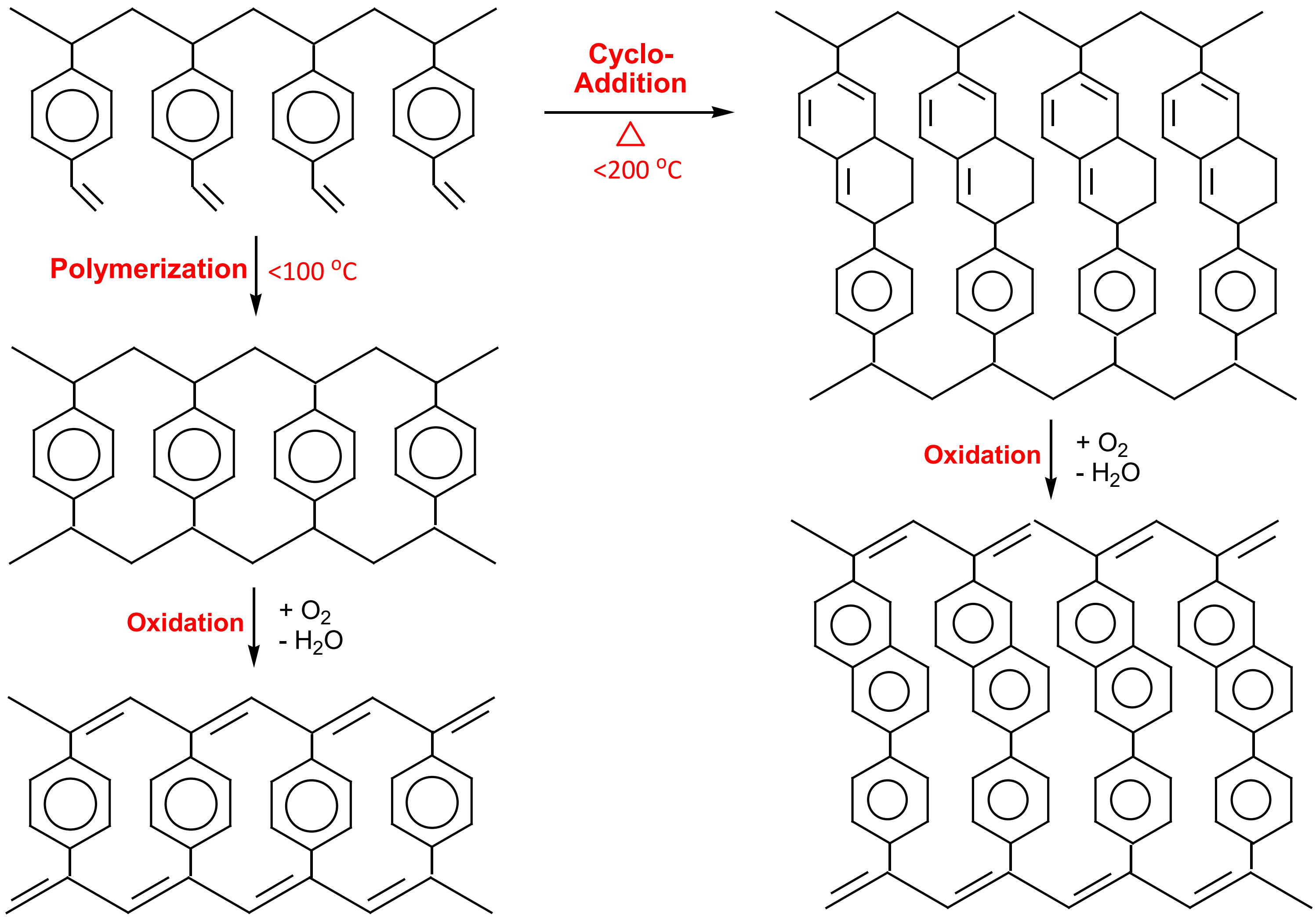
DVB monomer



PDVB polymer precursor



Approach: Stabilization mechanism (by heat)



- **Low temp. stabilization reactions via styrenyl side groups.**
- **Both reaction mechanism s require no external reagent.**

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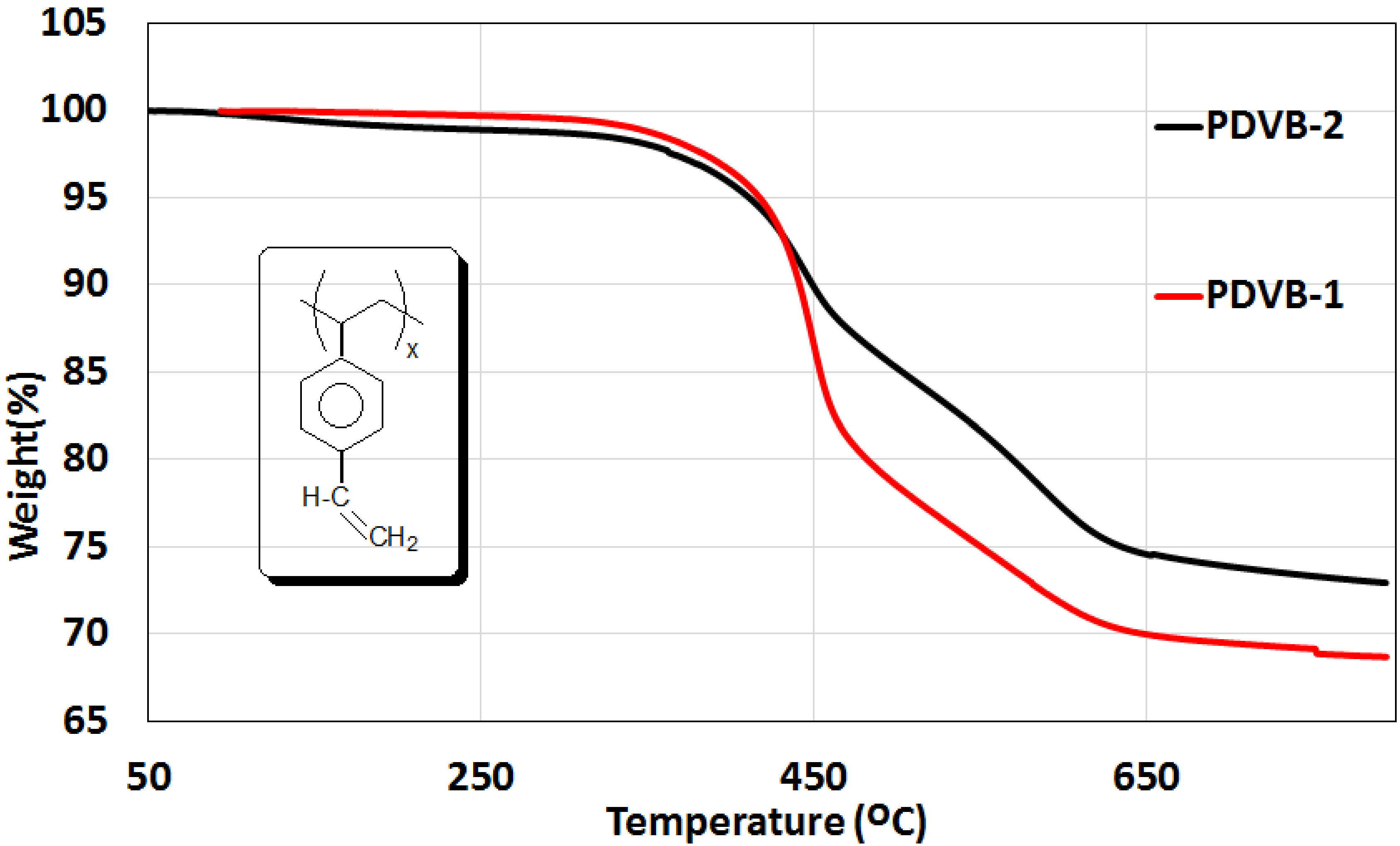
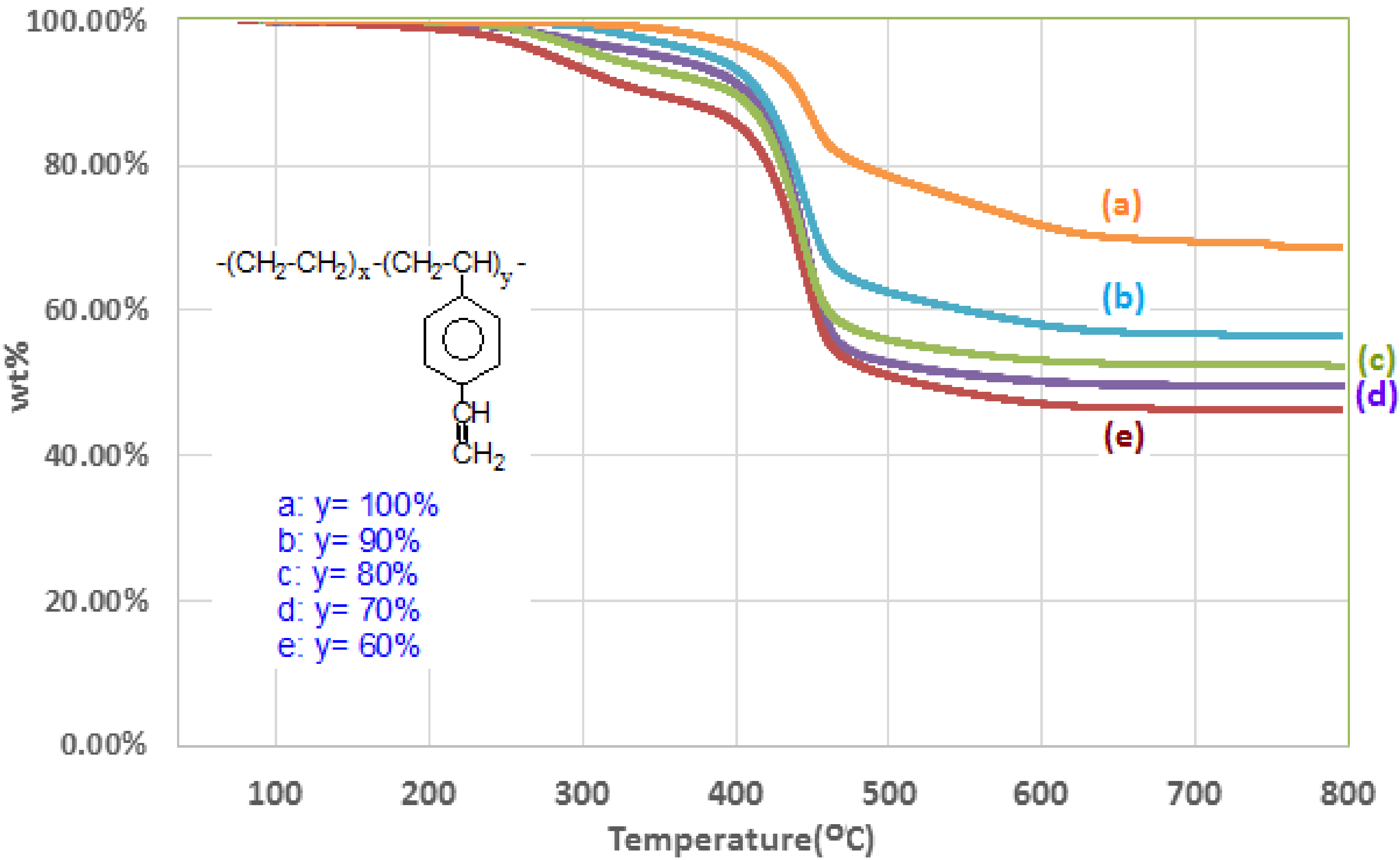
Accomplishments: TGA curves of PDVB precursors



Carbonization yield is in the range of 65-75%

Accomplishments: TGA curves of PDVB precursors



C yield systematically decreases with the decrease of DVB content

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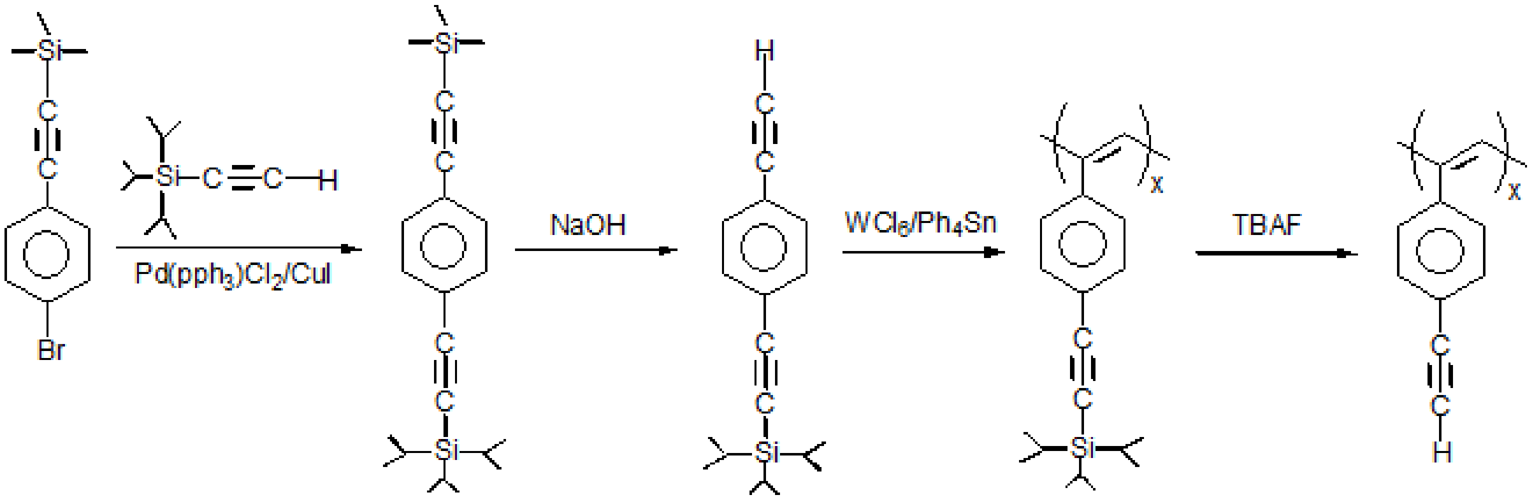
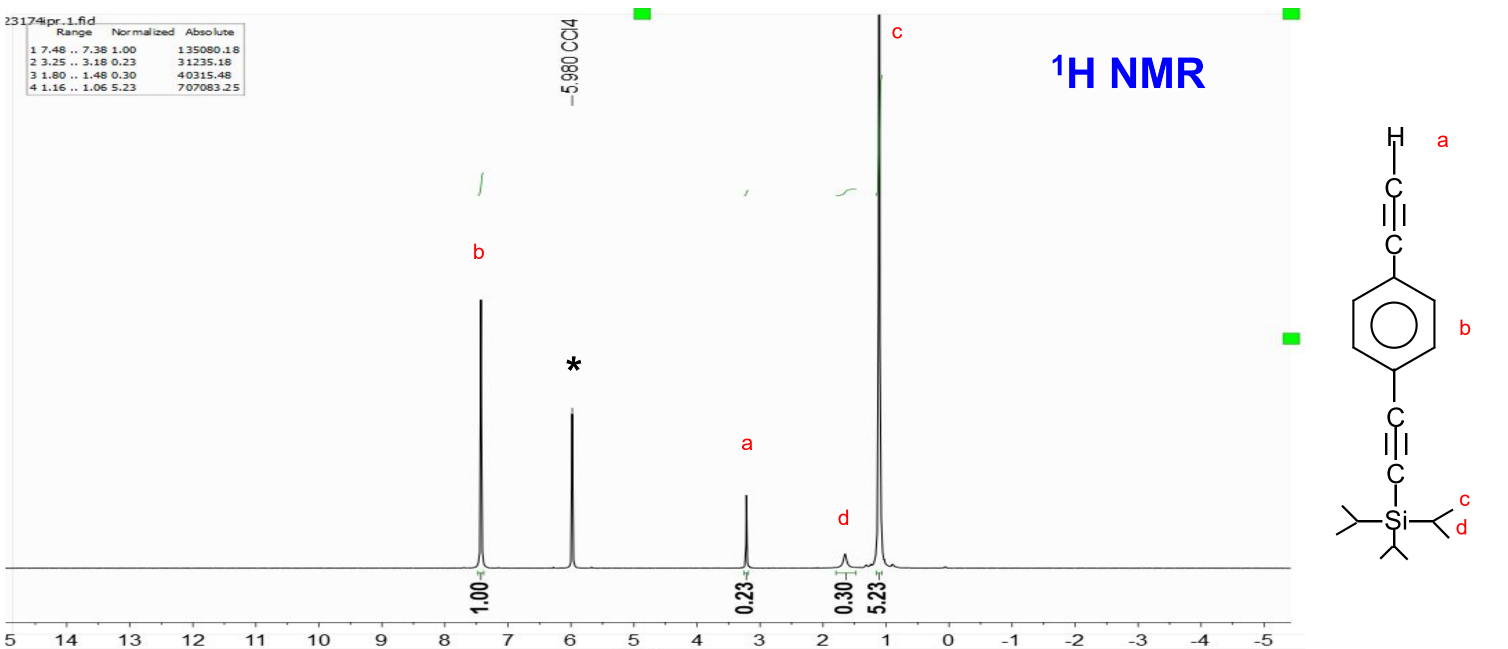
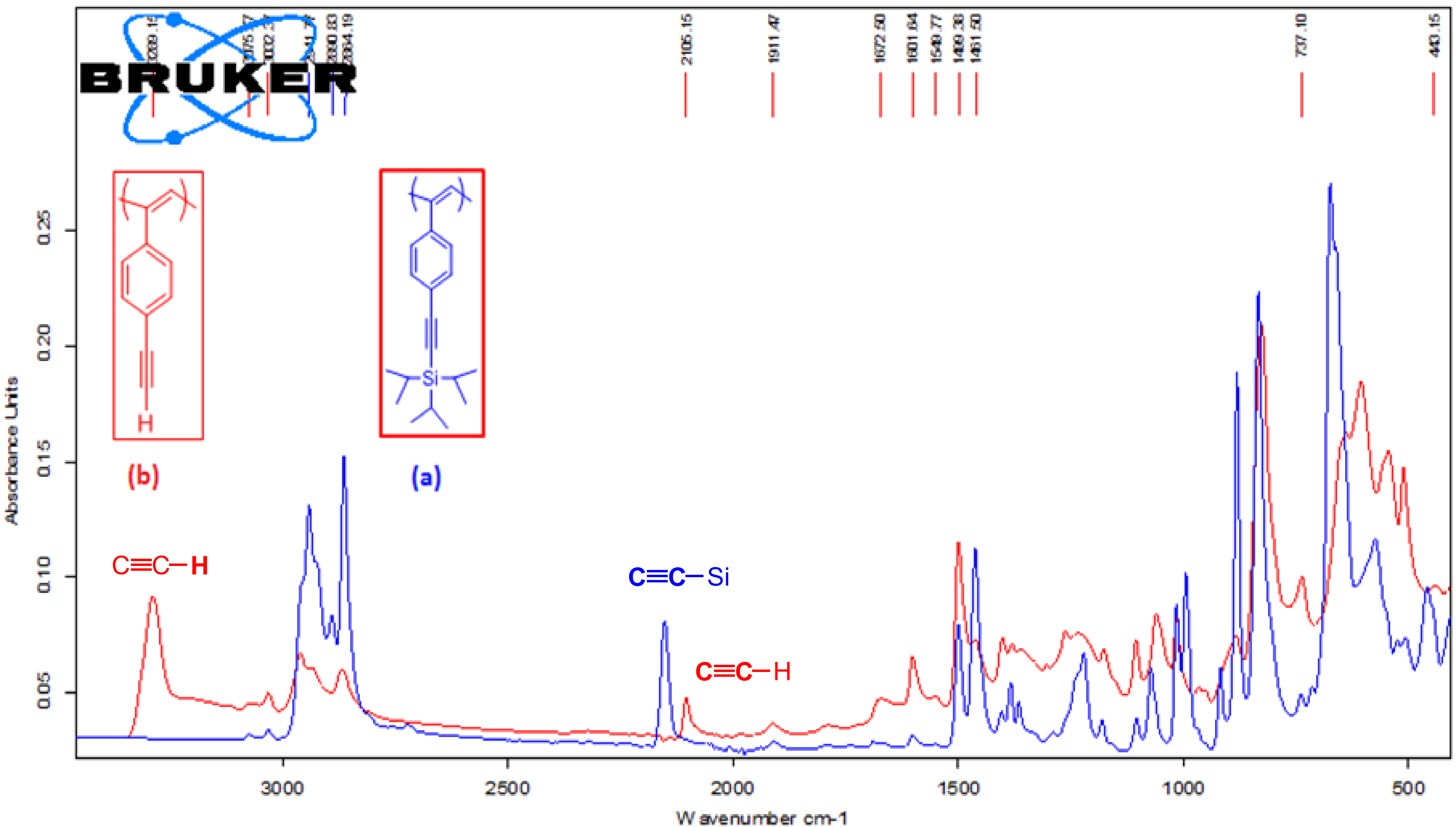
Accomplishments: Synthesis of Poly(phenylacetylene) derivatives

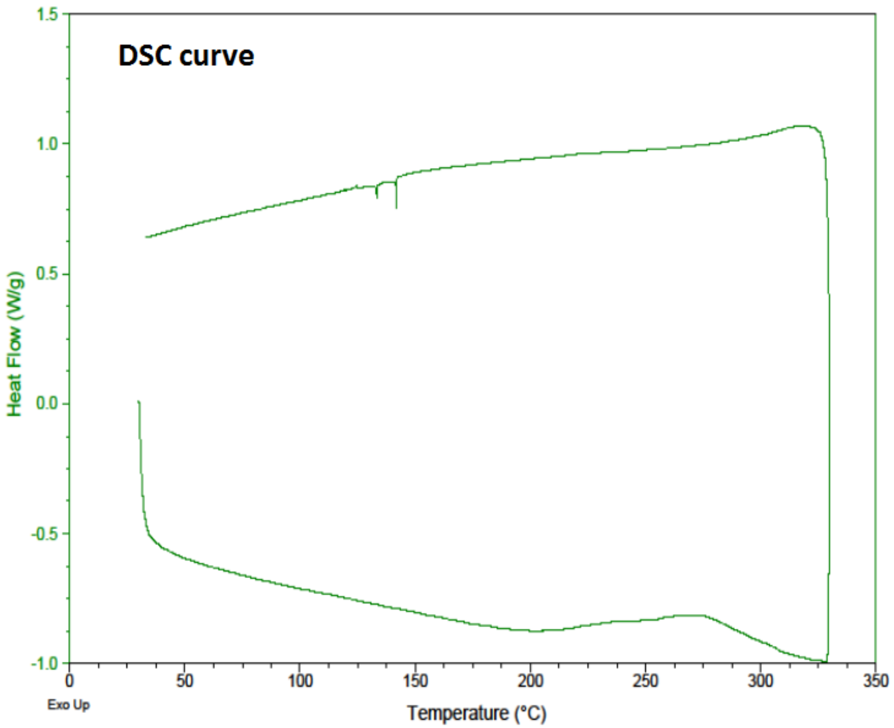


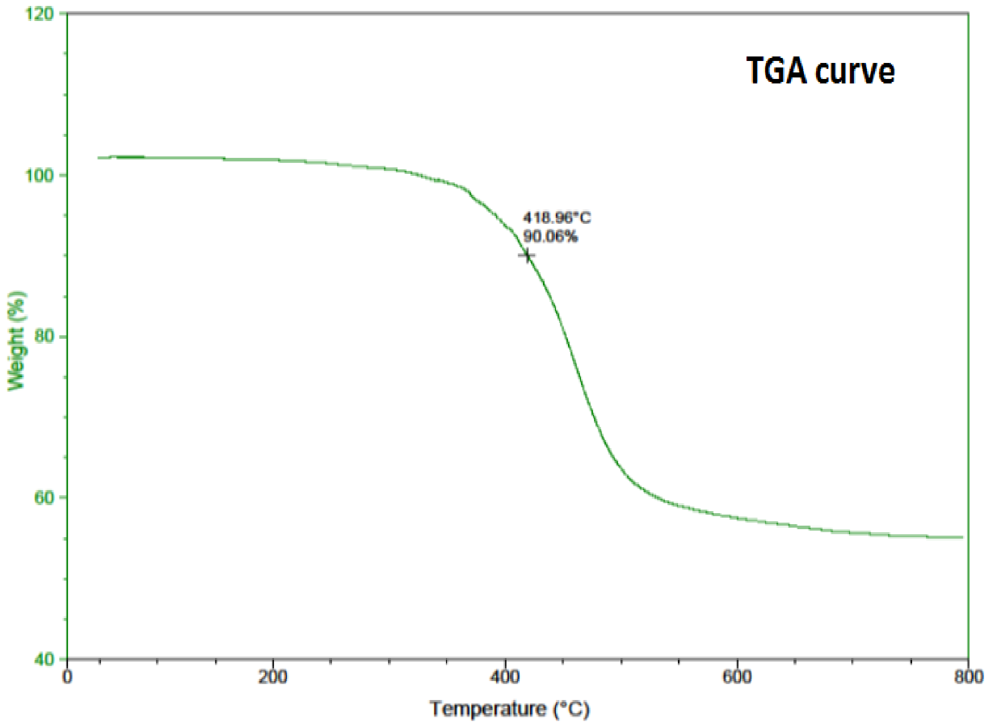


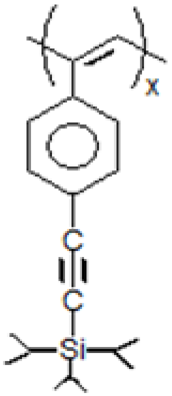
Accomplishments: FTIR spectra of Poly(phenylacetylene) derivatives



Accomplishments: DSC and TGA curves of Poly(phenylacetylene) acetylsilane-derivatives

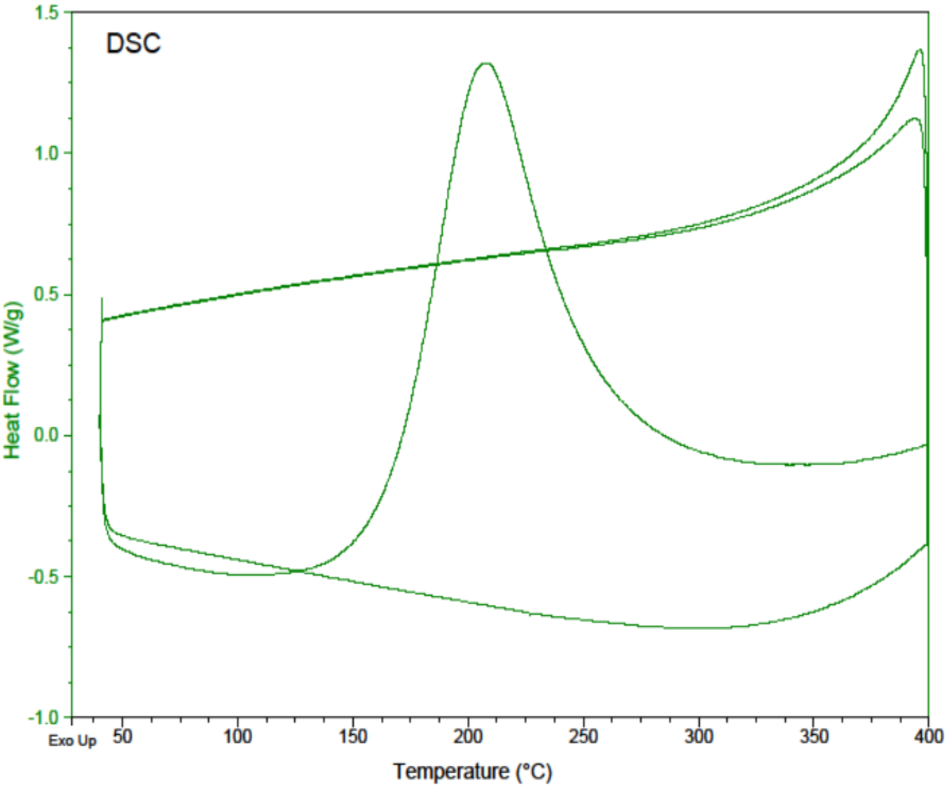


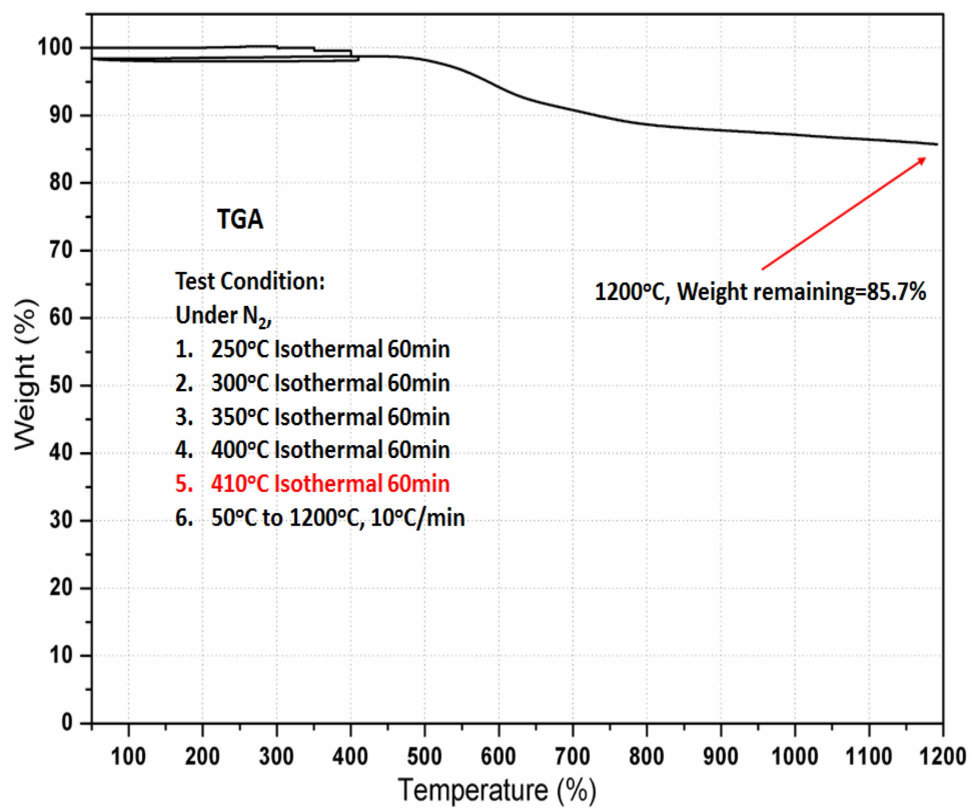


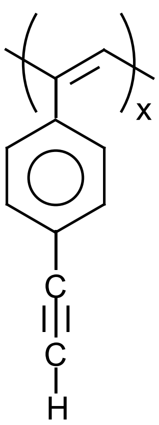


- Relatively weak stabilization reaction
- Stabilization at >250 °C
- Carbonization yield ~55%

Accomplishments: DSC and TGA curves of Poly(phenylacetylene) acetyl-derivatives







- **Strong well-defined stabilization mechanism**
- **Stabilization at 200-220 °C**
- **Carbonization yield ~85%**

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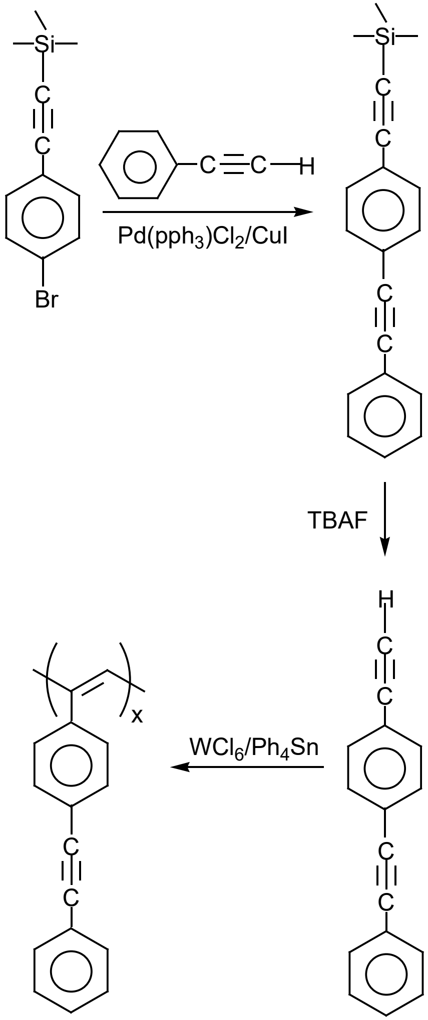
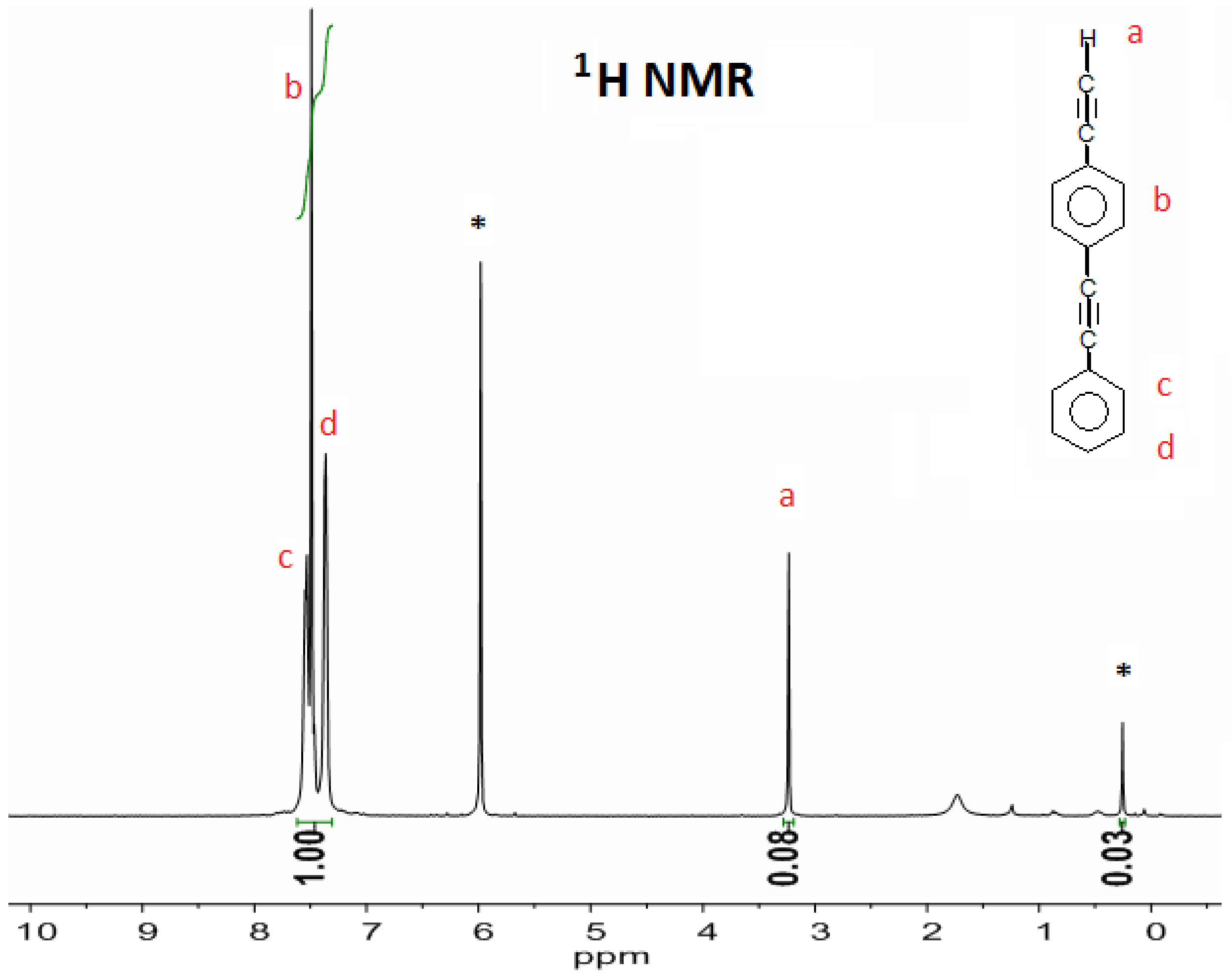
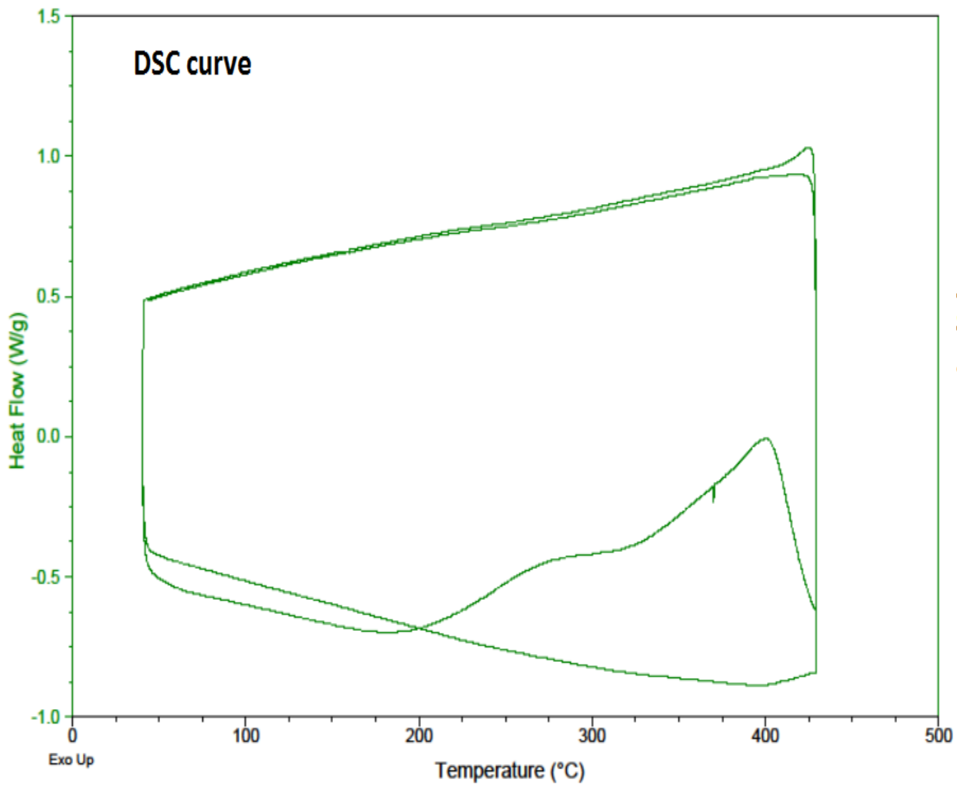
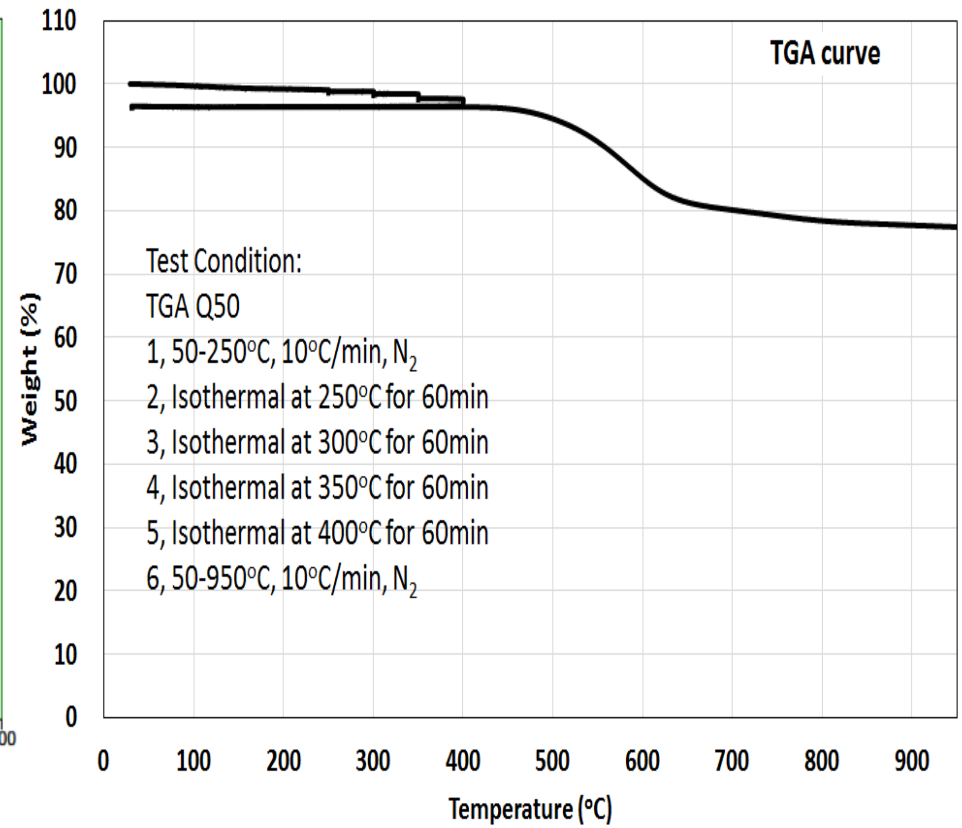
Accomplishments: Synthesis of Poly(phenylacetylene) acetylphenyl derivatives

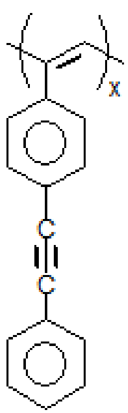




Accomplishments: DSC and TGA curves of Poly(phenylacetylene) acetylphenyl-derivative







- **Multiple stabilization mechanisms**
- **Stabilization happened at >250 °C**
- **Carbonization yield >75%**

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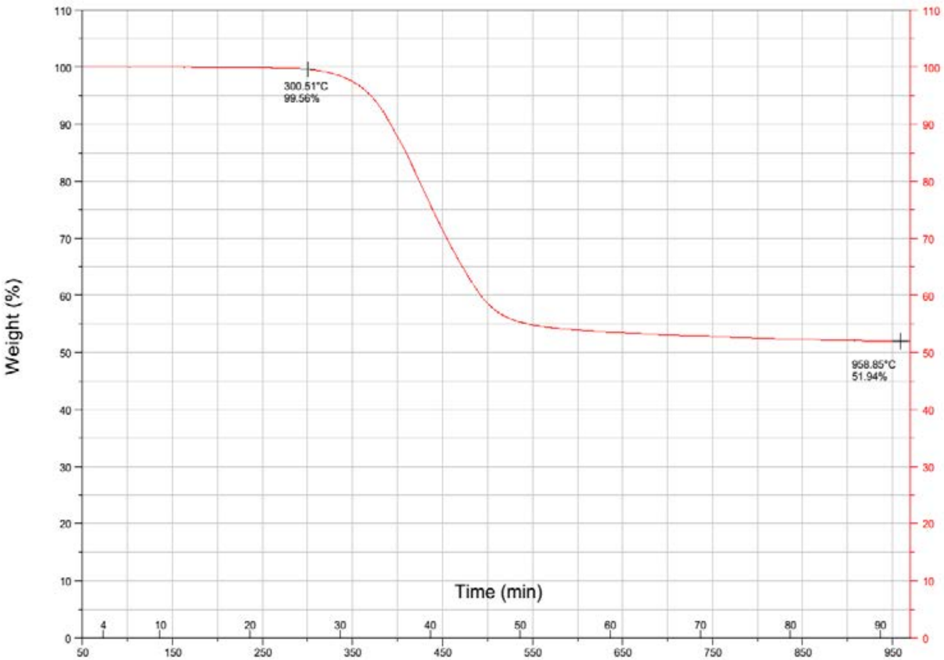
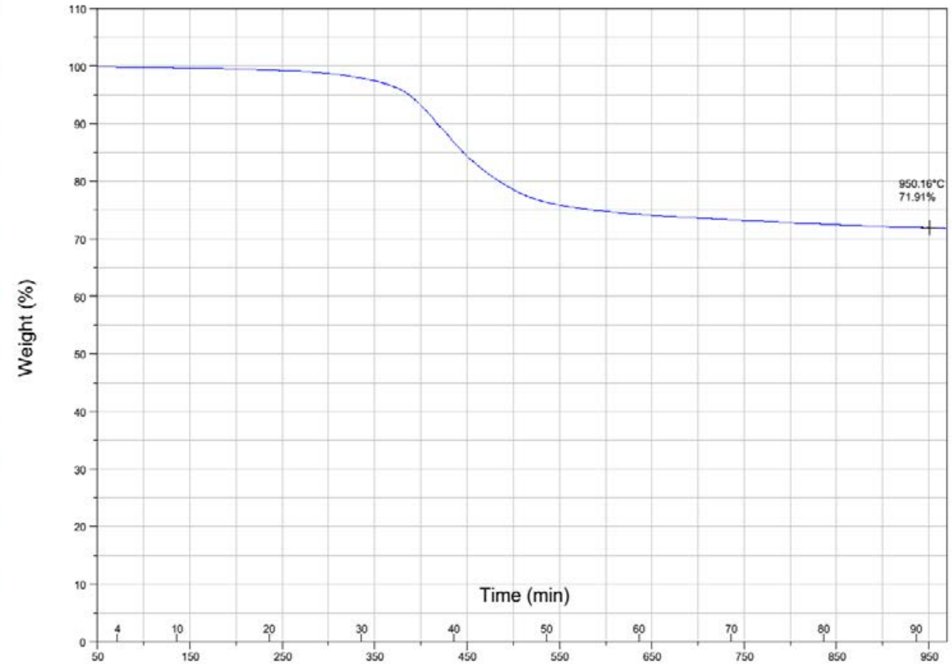
Accomplishments: Co-carbonization between Petroleum pitch and B-precursor

DSC curve comparison

Petroleum pitch



Petroleum pitch/B-precursor (1/1)



- **B elements incorporated in pitch in forming mesophase B-pitch precursor**
- **B enhances carbonization process**
- **Increase carbonization yield**

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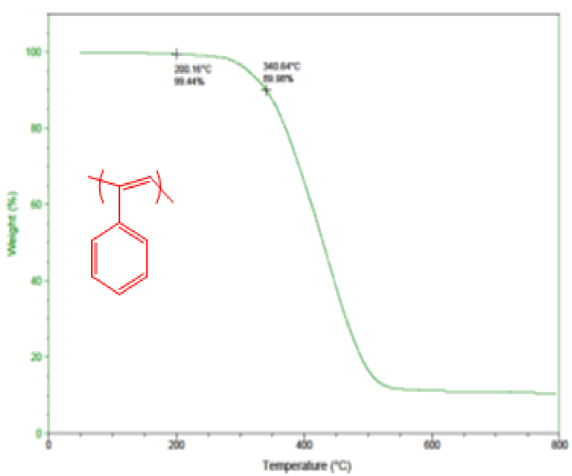
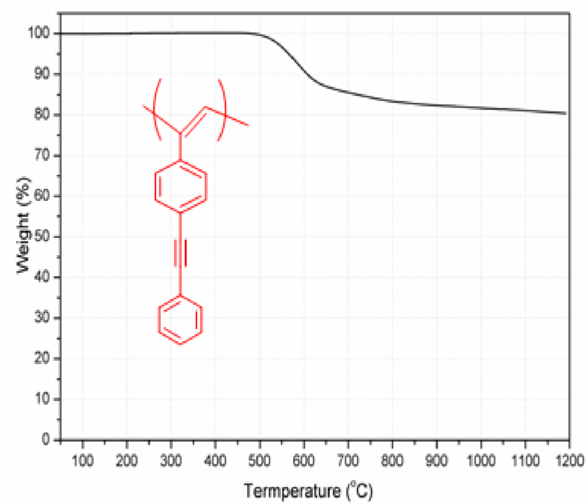
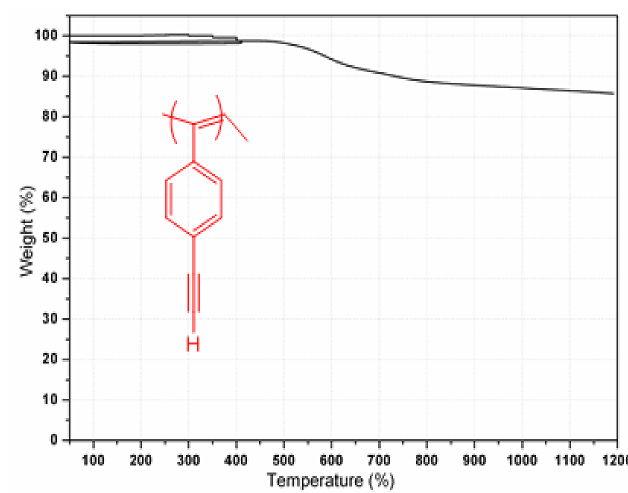
Summary

- **Conducting a systematical study (design, synthesis, and evaluation) to identify the suitable polymers with high carbonization yield.**
- **Two poly(phenylacetylene) derivatives show carbonization yield higher than 80%.**
- **Synthesis of B-containing pitch precursor that enhances the carbonization process.**
- **Collaborating with ORNL in fiber processing, thermal conversion, and carbon fiber evaluation.**







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Future Work

Milestone Summary Table							
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Project Title:		Developing A New Polyolefin Precursor for Low-Cost, High-Strength Carbon Fiber					
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Any proposed future work is subject to change based on funding levels