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

Project ID: ST147

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2019 DOE Hydrogen Program Annual Merit Review
April 29-May 1, 2019

Overview

Timeline

- Project start date: 9/1/2017
- Project end date: 8/31/2020
- % complete: 60%

Budget

- Total project funding: $931,643

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

- Funding for FY2018-19: $ 316,788
- Go/no-Go decision: Pass in Sept. 2018

Barriers

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

Partners

- LightMat consortium
- Oak Ridge National Lab.

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)

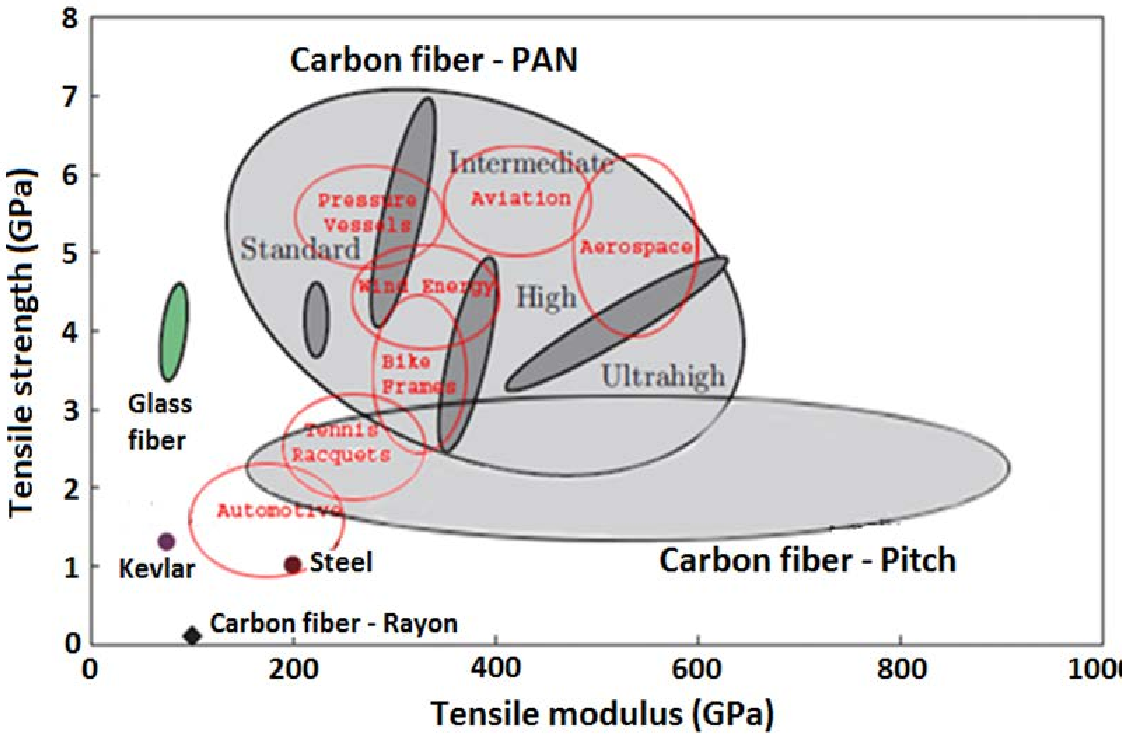
Composite overwrapped pressure vessel for 5.6 Kg usable hydrogen

	Energy cost ($/kWh)	System cost ($/vehicle)
2013 system	$17	$3,200
2015 system	$15	$2,800
DOE Target	$10	$1,900

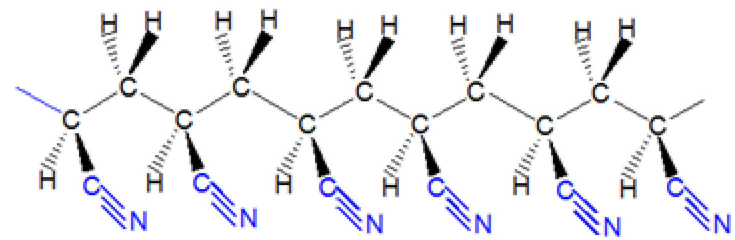
Type IV COPV system with polymer liner and annual production rate of 500,000 systems

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

Relevance: Tensile Properties

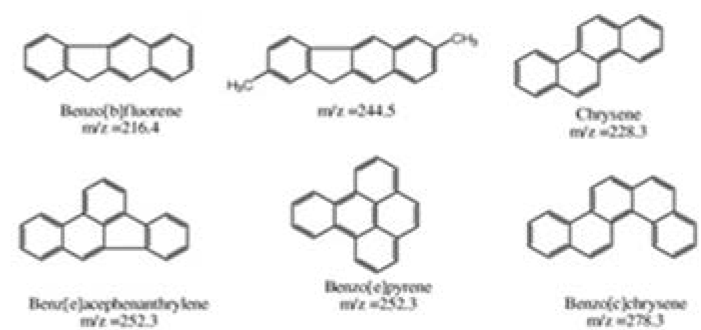


PAN Polymer



Pitch from petroleum or coal tar

(PAH mixture with Mw. 200-800 g/mole)



PAN precursor

Advantages:

Applied tension during the conversion

Low defects, Good alignment, High strength

Disadvantages:

High cost, Wet-spinning, Low C yield (50%)

Pitch precursor

Advantages of Pitch precursor:

Low cost, melt-spinning, high C yield (up to 70%)

Disadvantages:

No applied tension during the conversion

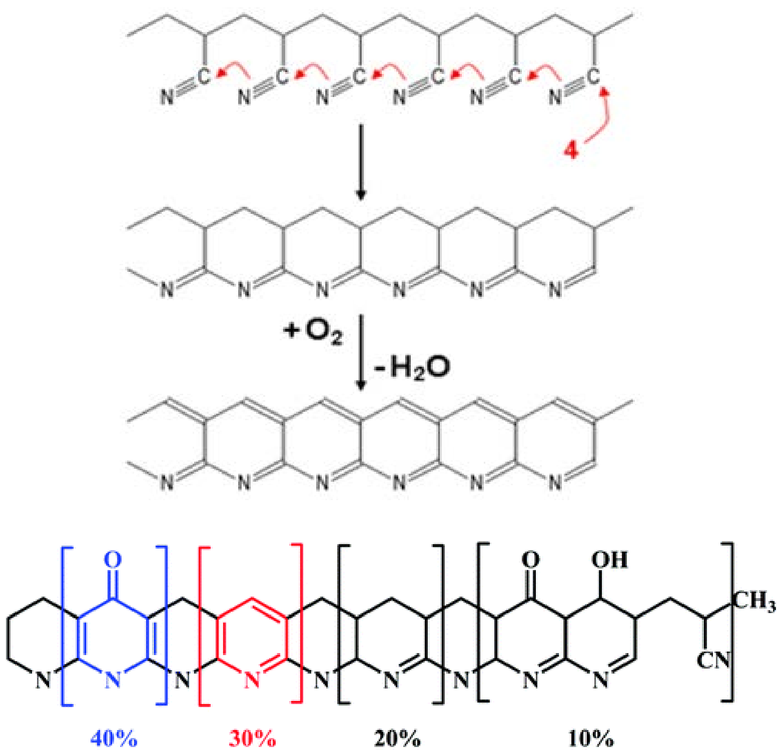
High defects, Poor alignment, Low strength

How to design a precursor with the combined advantages?

Relevance: PAN thermal conversion

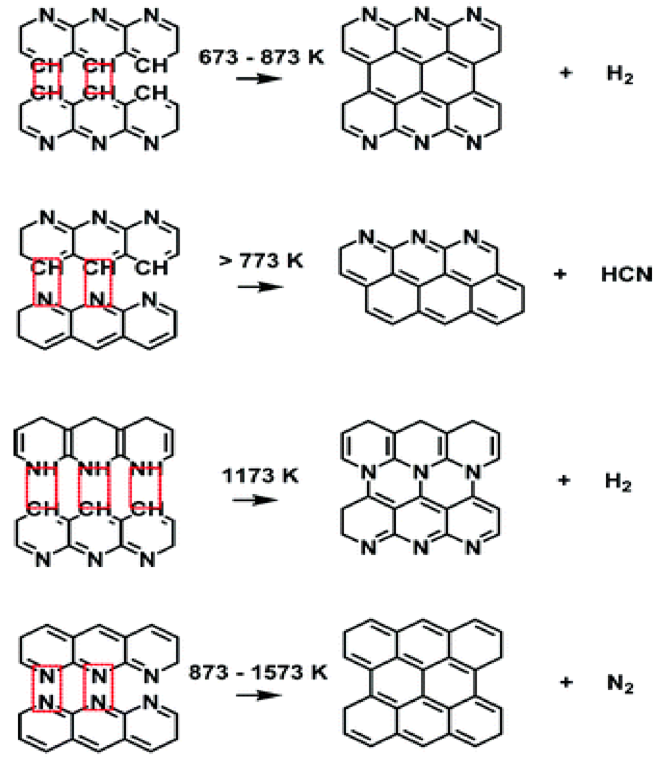
Stabilization

(200-300 ^oC in Air)



Carbonization

(1000-2000 ^oC under N_2)

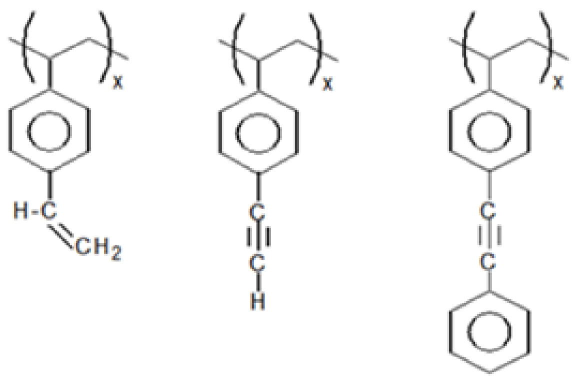


Low C yield is mostly due to the drive-off all N, O, and H heteroatoms.

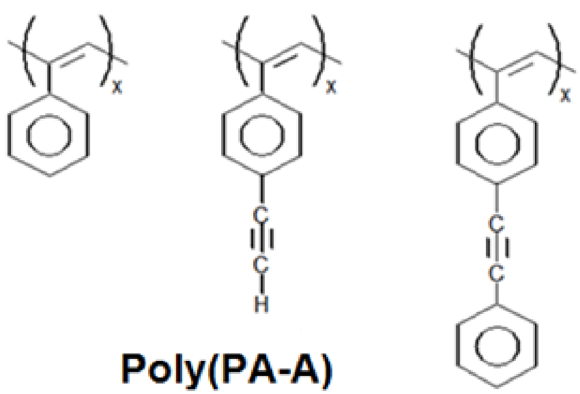
Design new <u>pure hydrocarbon polymer</u> precursor that is reactive (crosslinking, cycloaddition, ring fusion, etc.) under N_2 atmosphere.

Approach: New hydrocarbon polymer precursors

Polyethylene (PE) Backbone

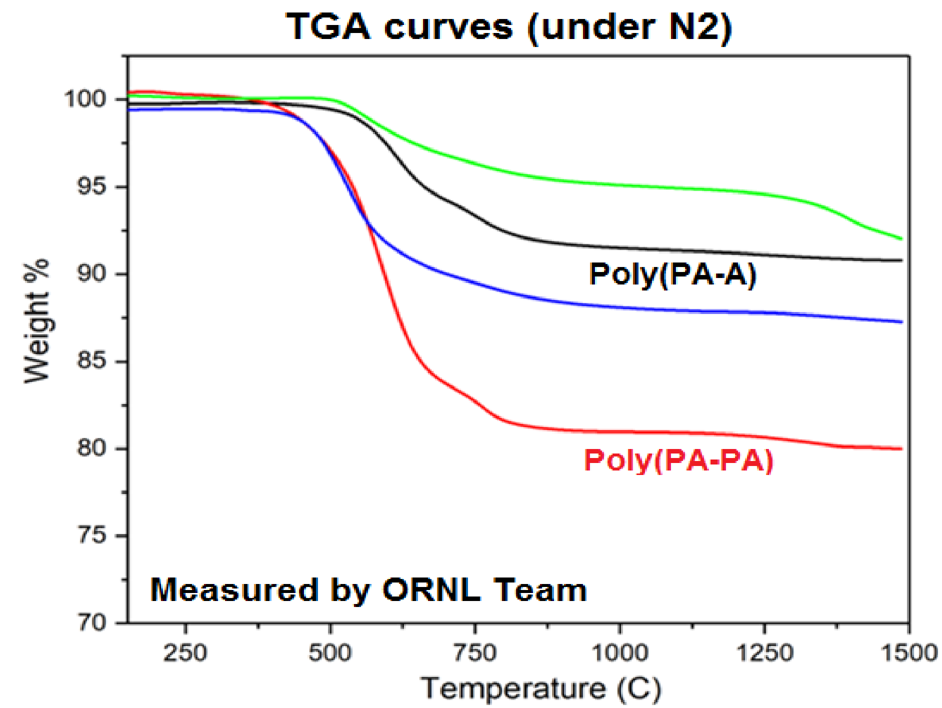


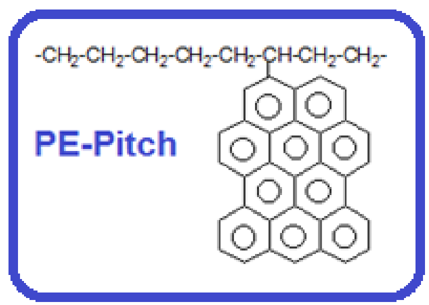
Polyacetylene (PA) Backbone

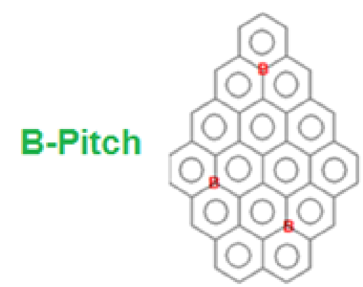


Poly(PA-A)

Poly(PA-PA)

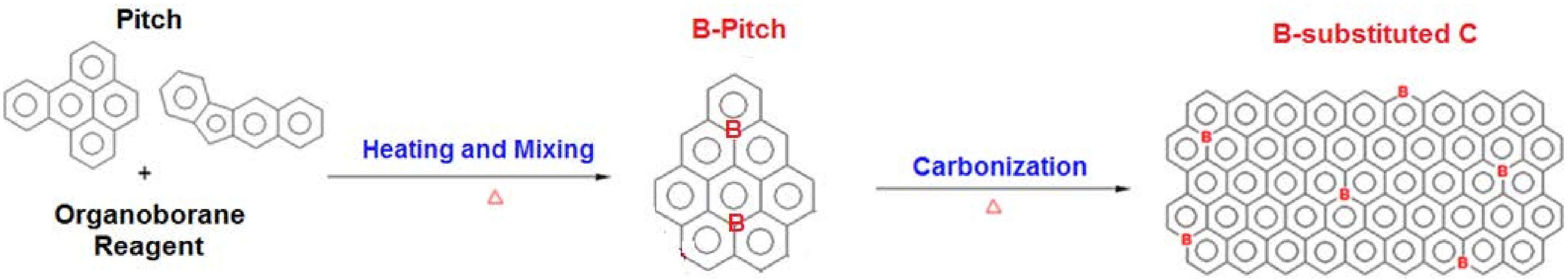


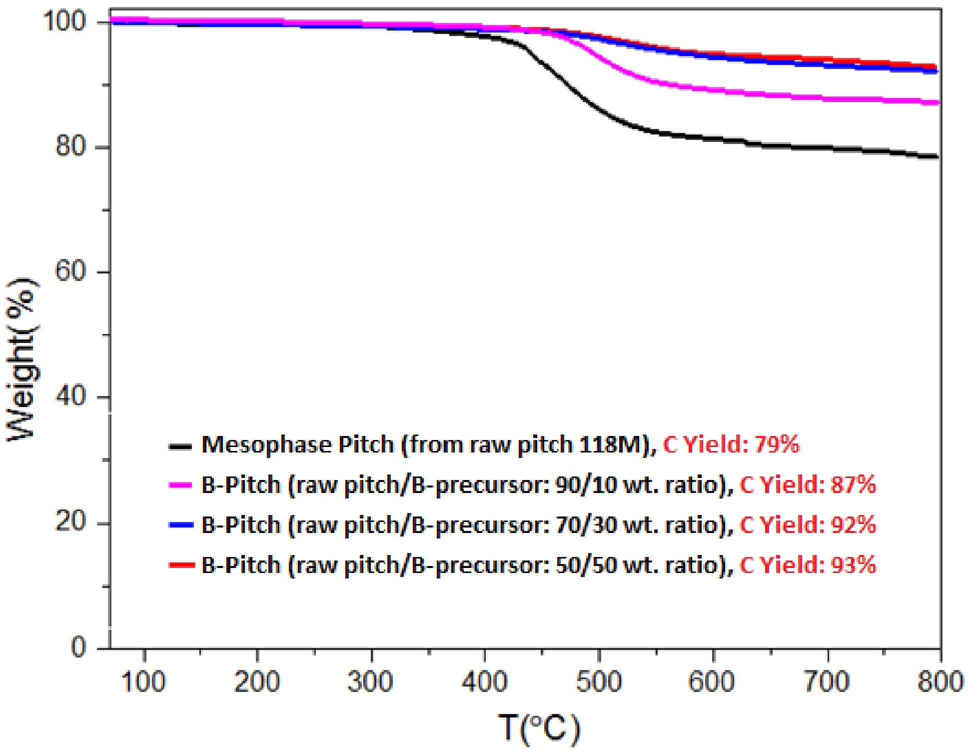


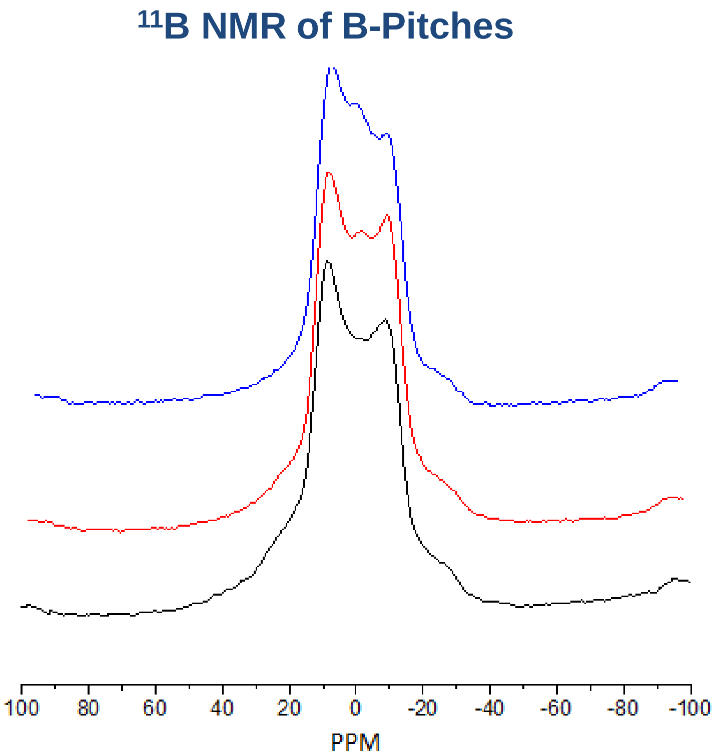


No O_2/stabilization step needed in the conversion process to Carbon. Most polymers are solution-processible, but not all melt-processing.

Accomplishments: B-containing pitch precursor

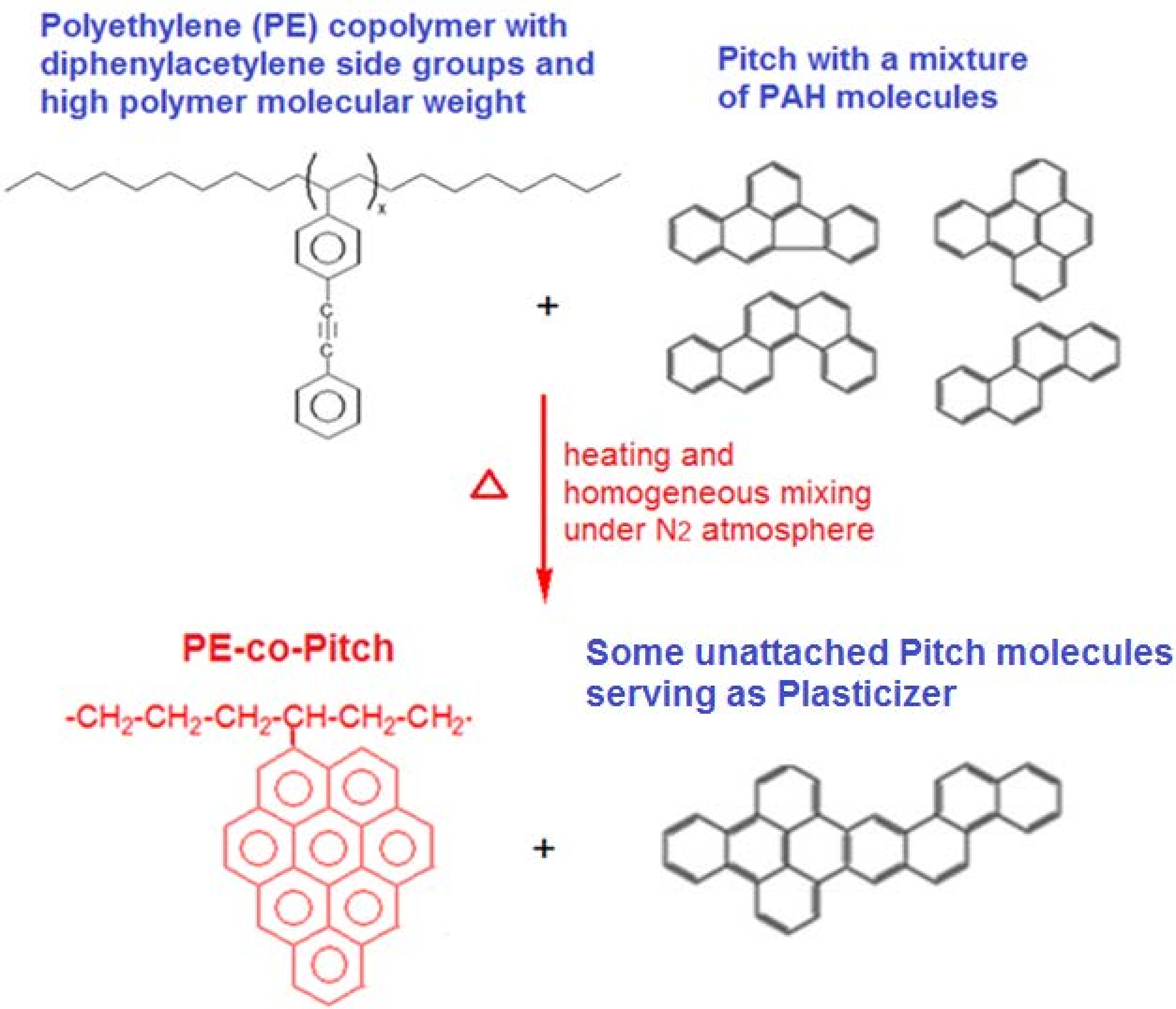






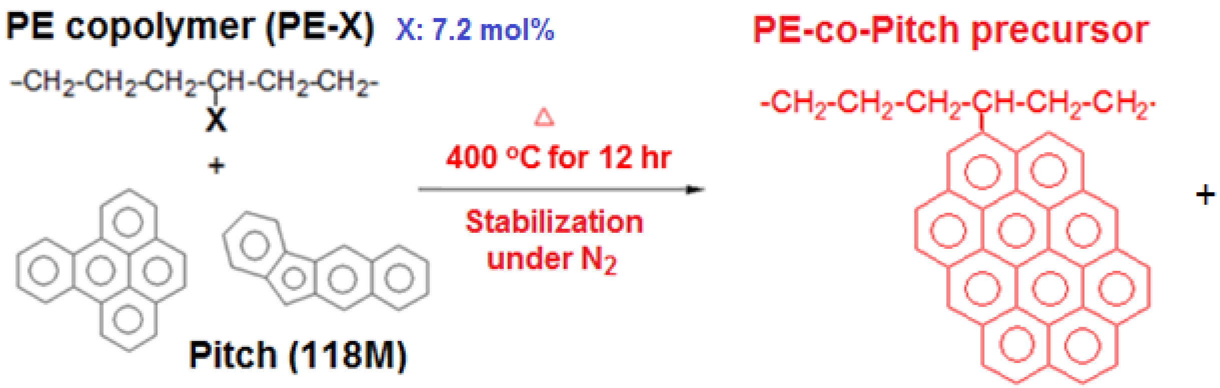
B catalyzes the carbonization process.

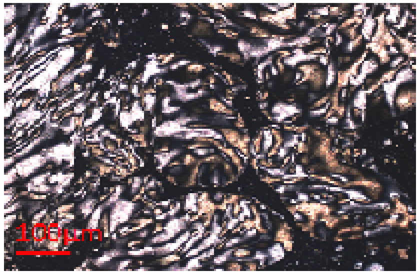
Approach: New PE-co-Pitch precursors



The resulting PE-co-Pitch precursor shall be melt-processible, if some potential side reactions can be minimized or prevented.

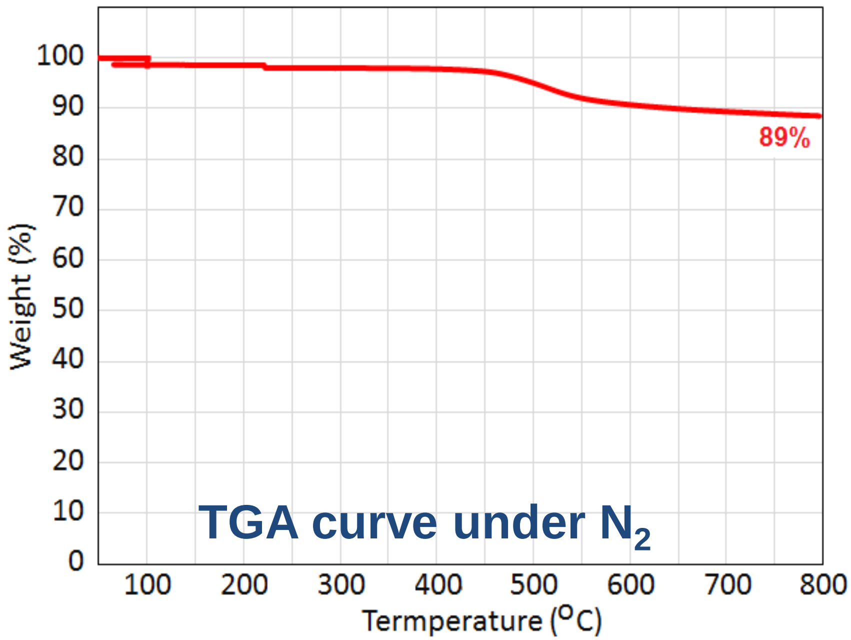
Accomplishments: PE-co-Pitch precursor (Mesophase)



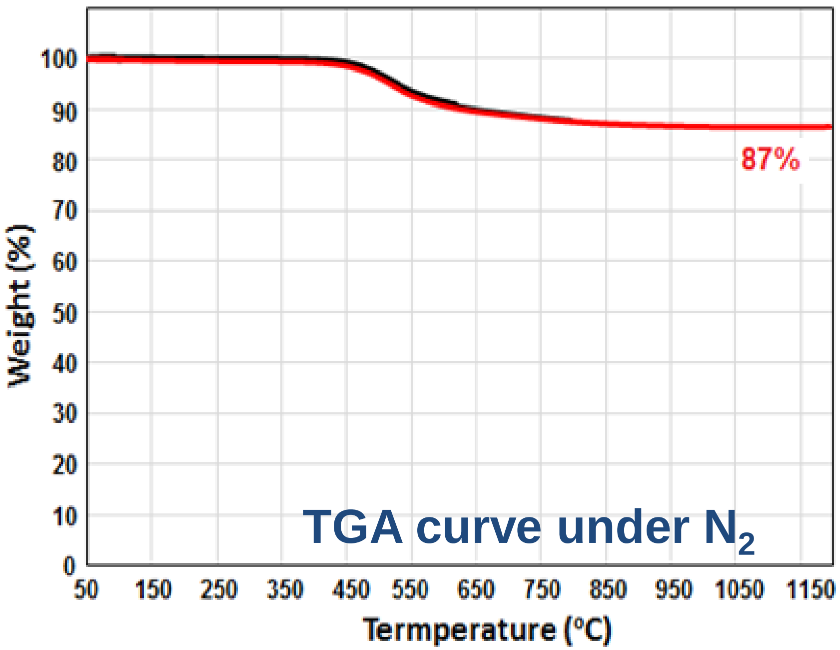


Mesophase Pitch

PE-X/Pitch: 10/90 wt. ratio

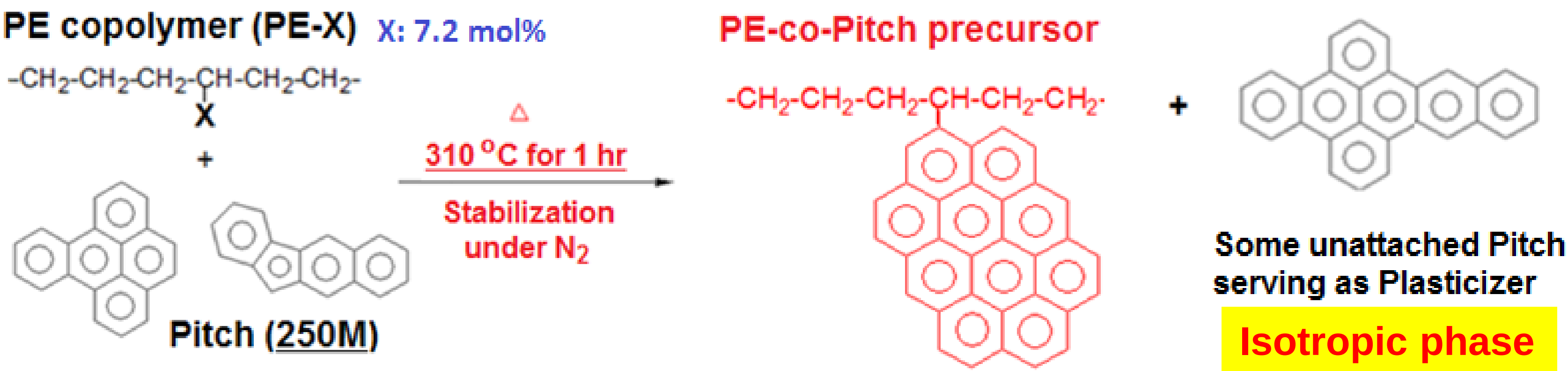


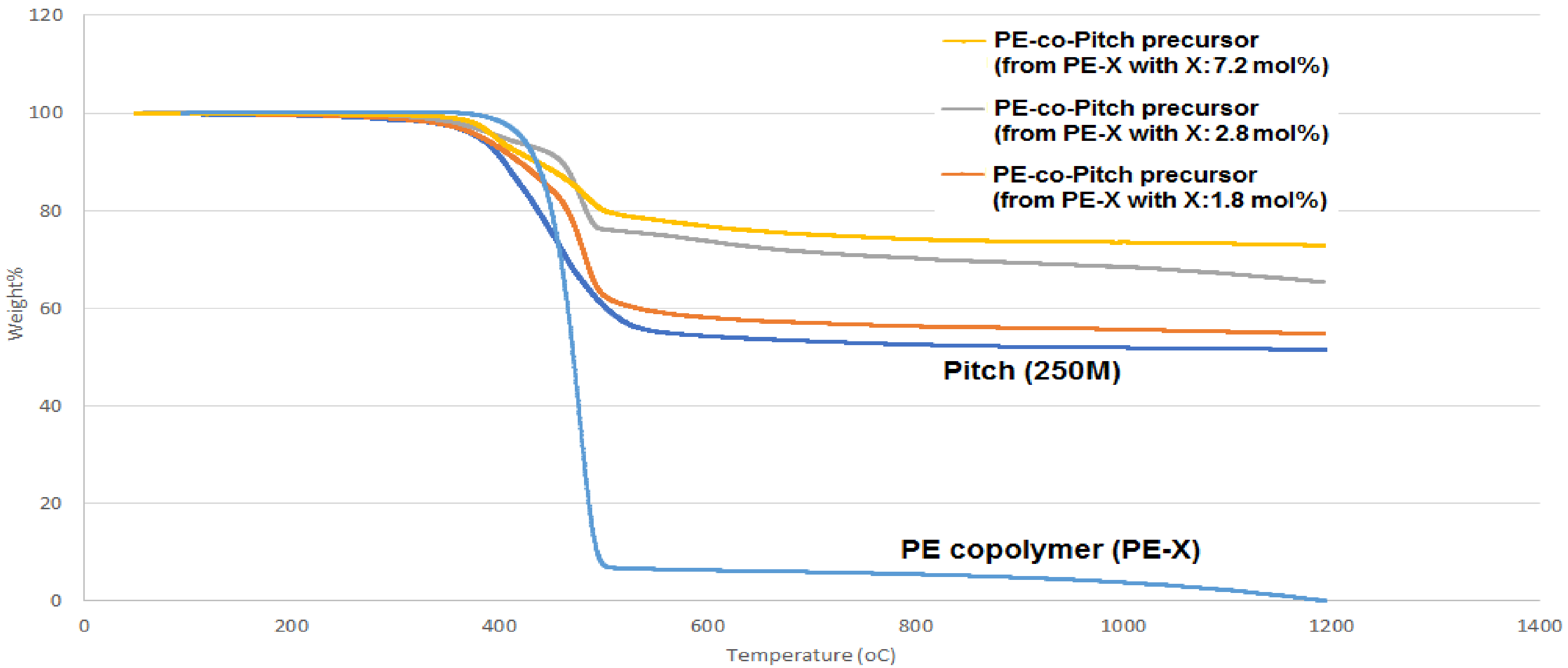
50/50 wt. ratio



The resulting mesophase PE-co-Pitch precursor is not melt-processible.

Accomplishments: PE-co-Pitch precursor (Isotropic phase)

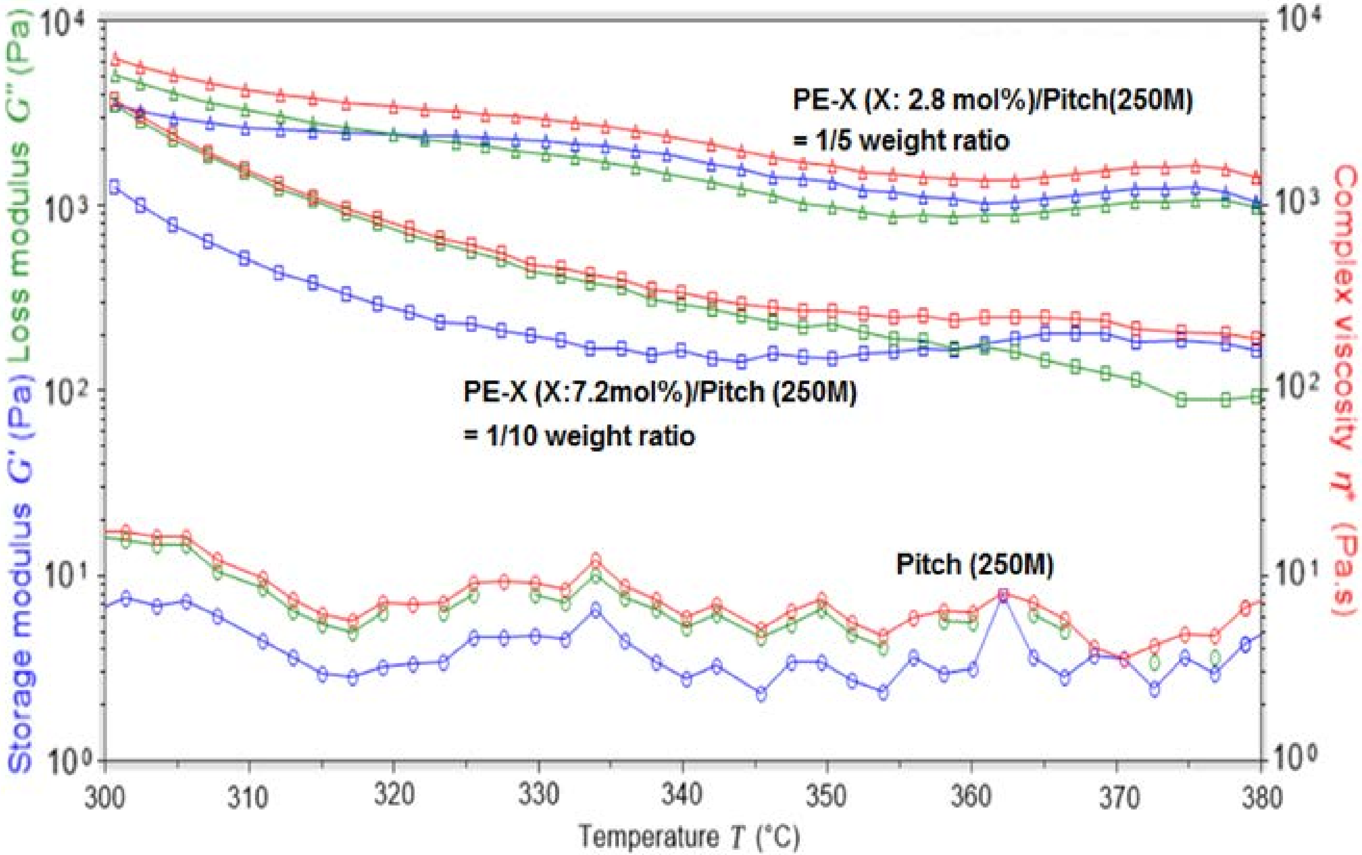




All PE-co-Pitch precursors show higher C yield than both PE-X and Pitch.

Accomplishments: Melt-processible PE-co-Pitch precursor

Oscillation Rheology (temperature sweep 10 °C/min)



Both PE-co-Pitch precursors exhibit complex viscosity in the typical range (100-5000 Pa.s) for melt-processing.

The PE-co-Pitch precursor (1/10 wt. ratio) shows a suitable processing temperature range between 320-340 °C.

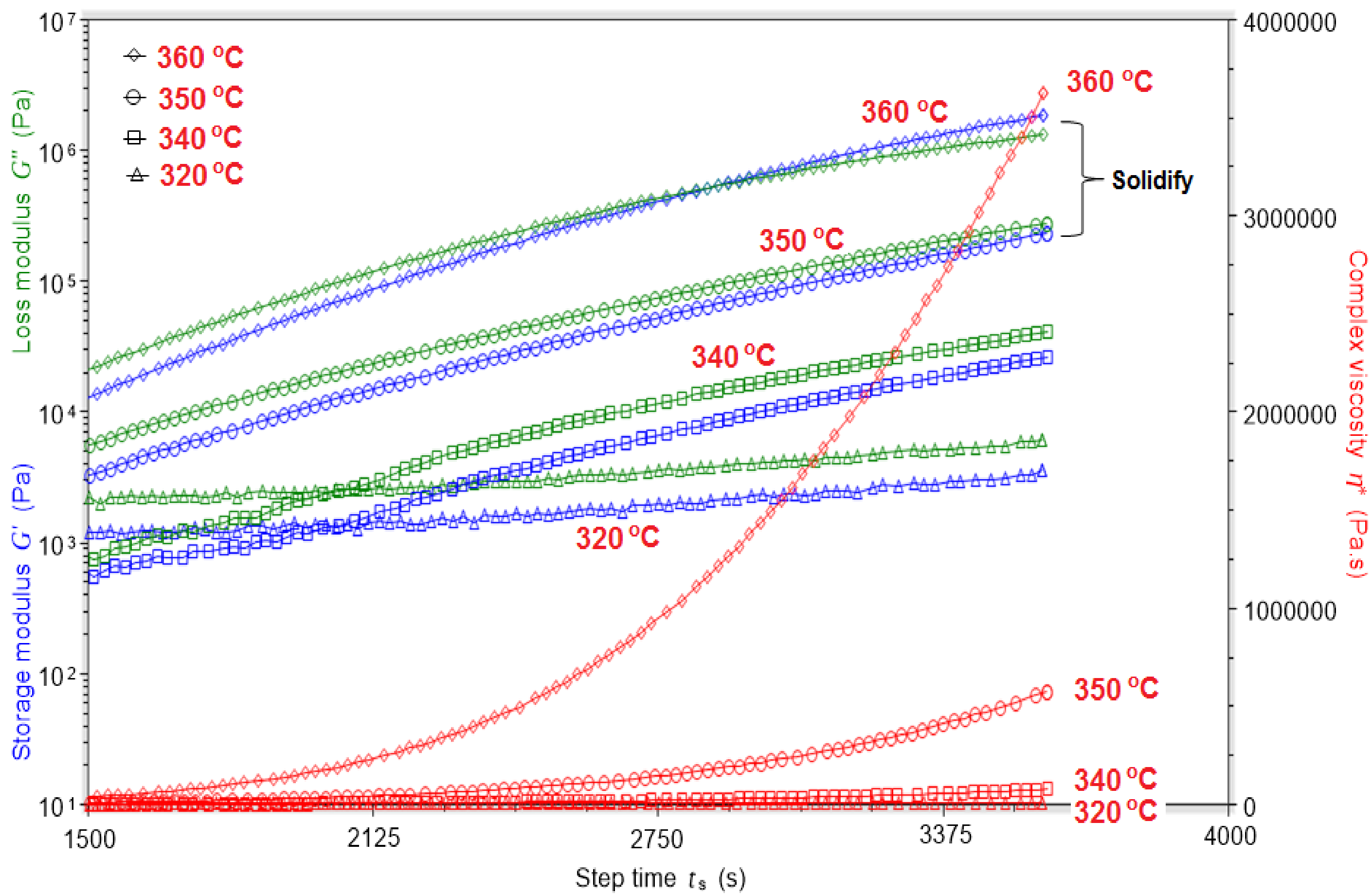
Accomplishments: Melt-processible PE-co-Pitch precursor

PE-X/Pitch(250M): (1/10 weight ratio)

PE-X copolymer (with 7.2 mol% X units)

Some unreacted Pitch (serving as plasticizer)

Oscillation Rheology (time sweep)

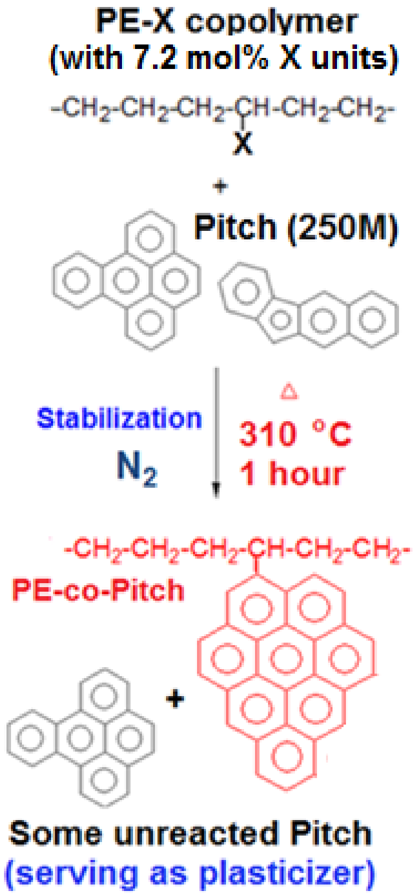


This PE-co-Pitch precursor shows a wide processing window at 320-340 °C range for about 1 hour.

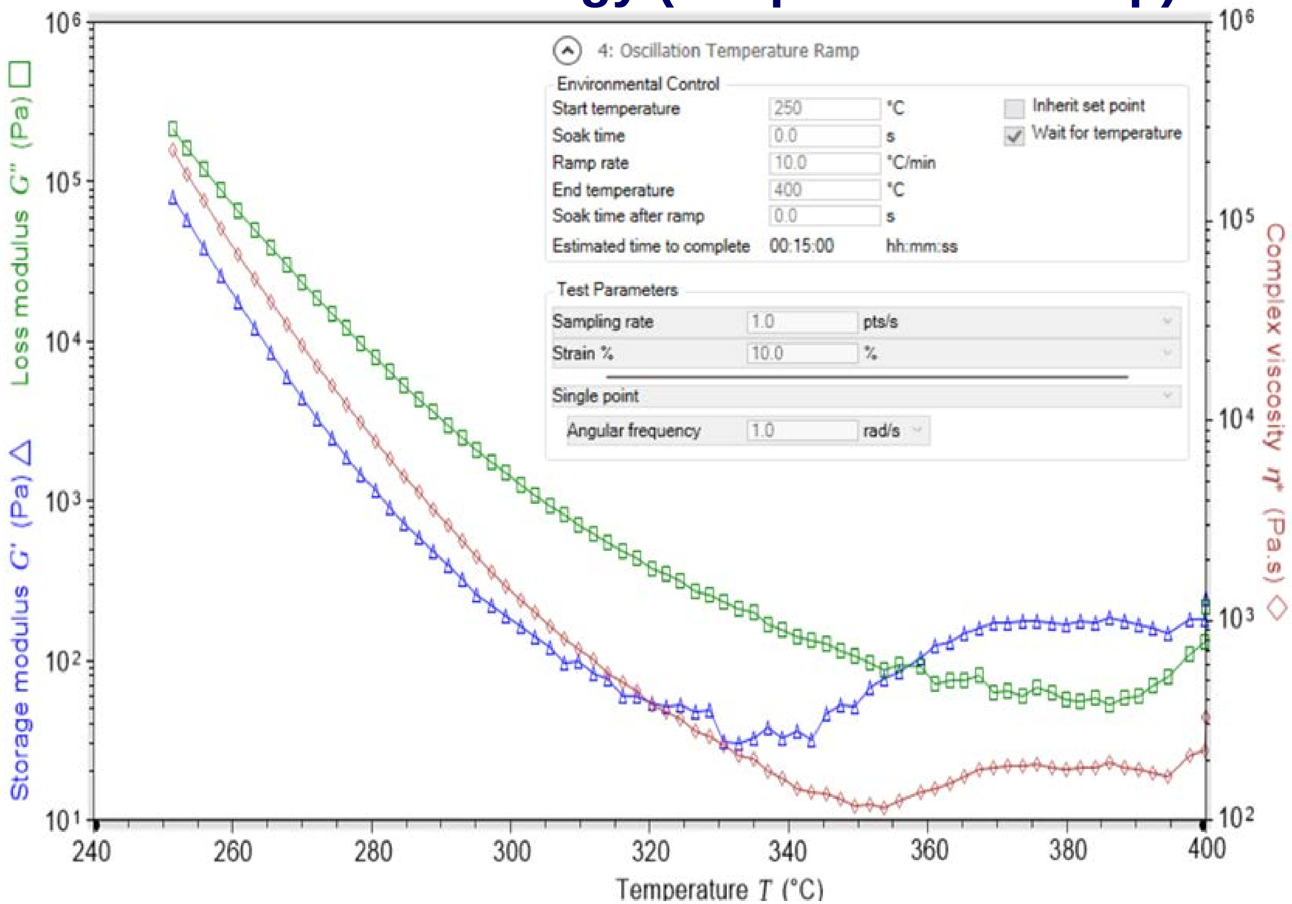
Accomplishments: Melt-processible PE-co-Pitch precursor

PE-X/Pitch(250M):
(1/10 weight ratio)

This PE-co-Pitch precursor was scaled up to 100g quantity and carried out the melt-spinning process at the ORNL facility.

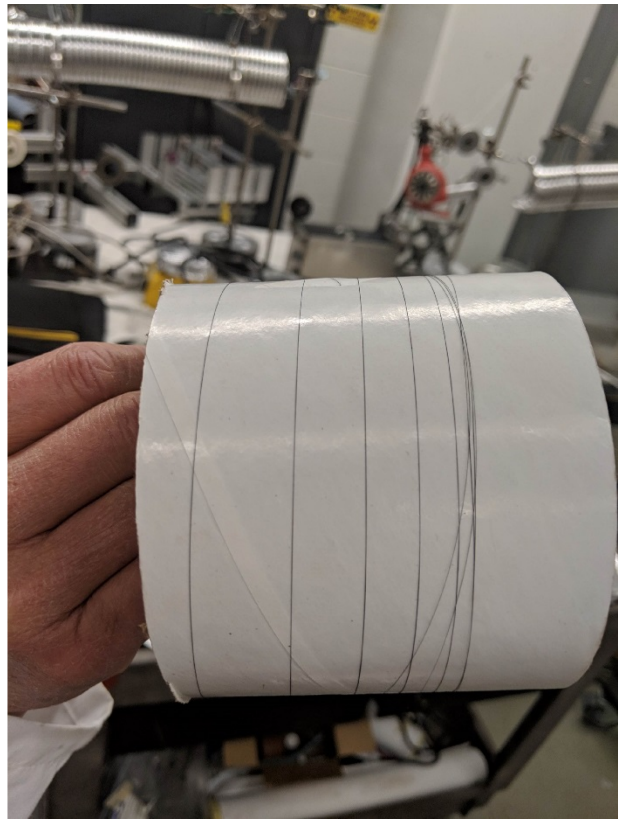


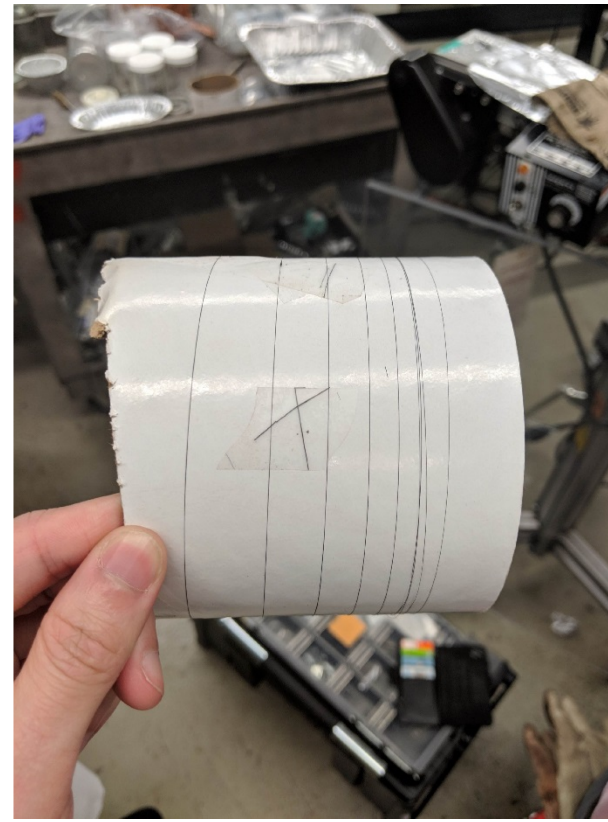
Oscillation Rheology (temperature sweep)



Accomplishments: Melt-spinning of PE-co-Pitch

Melt-spinning machine | **Fiber with low speed** | **Fiber with high speed**





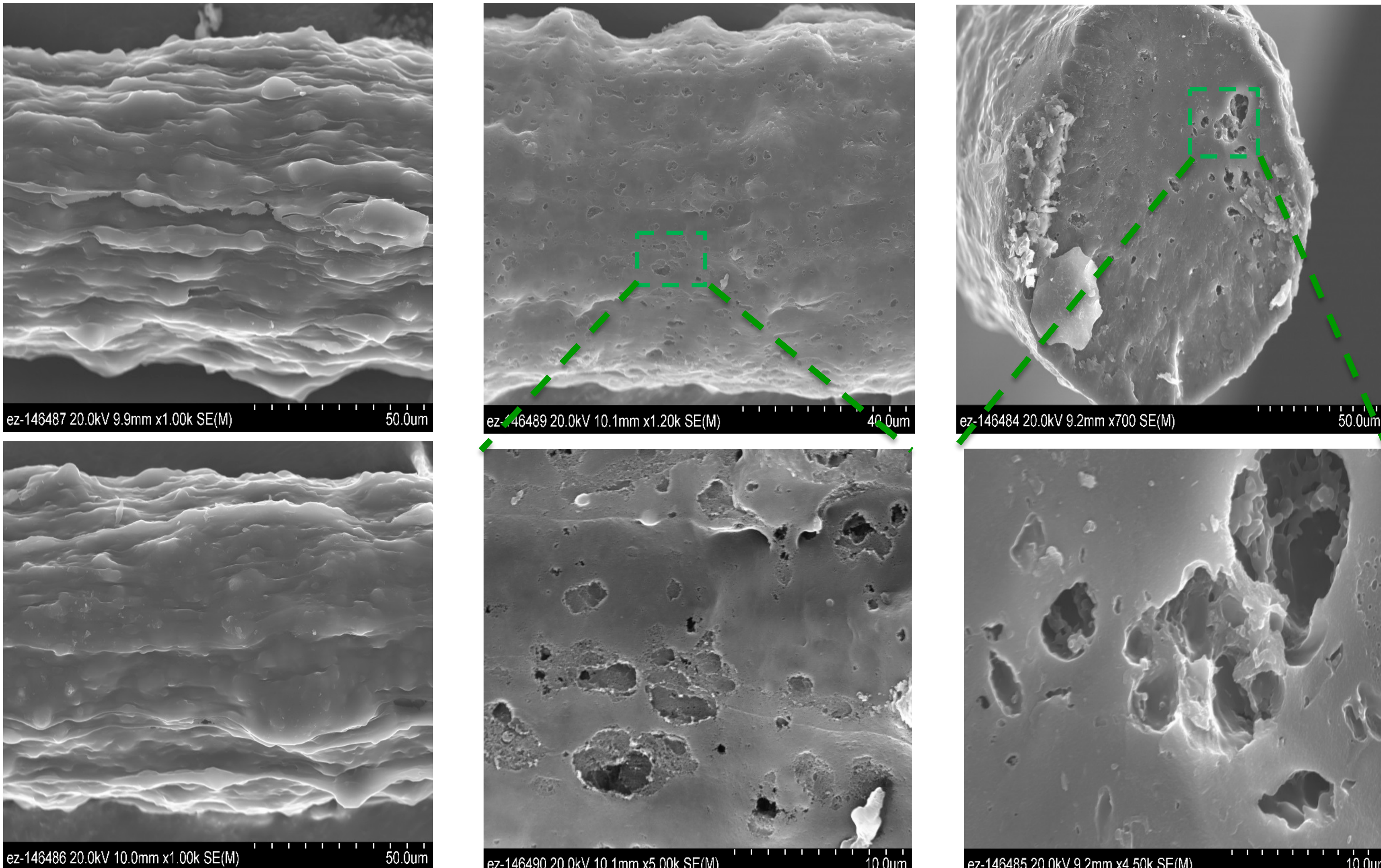
ORNL facility

https://youtu.be/H5eZN3dZhUU

Accomplishments: Carbon Fibers from PE-co-Pitch

(Results from ORNL team)

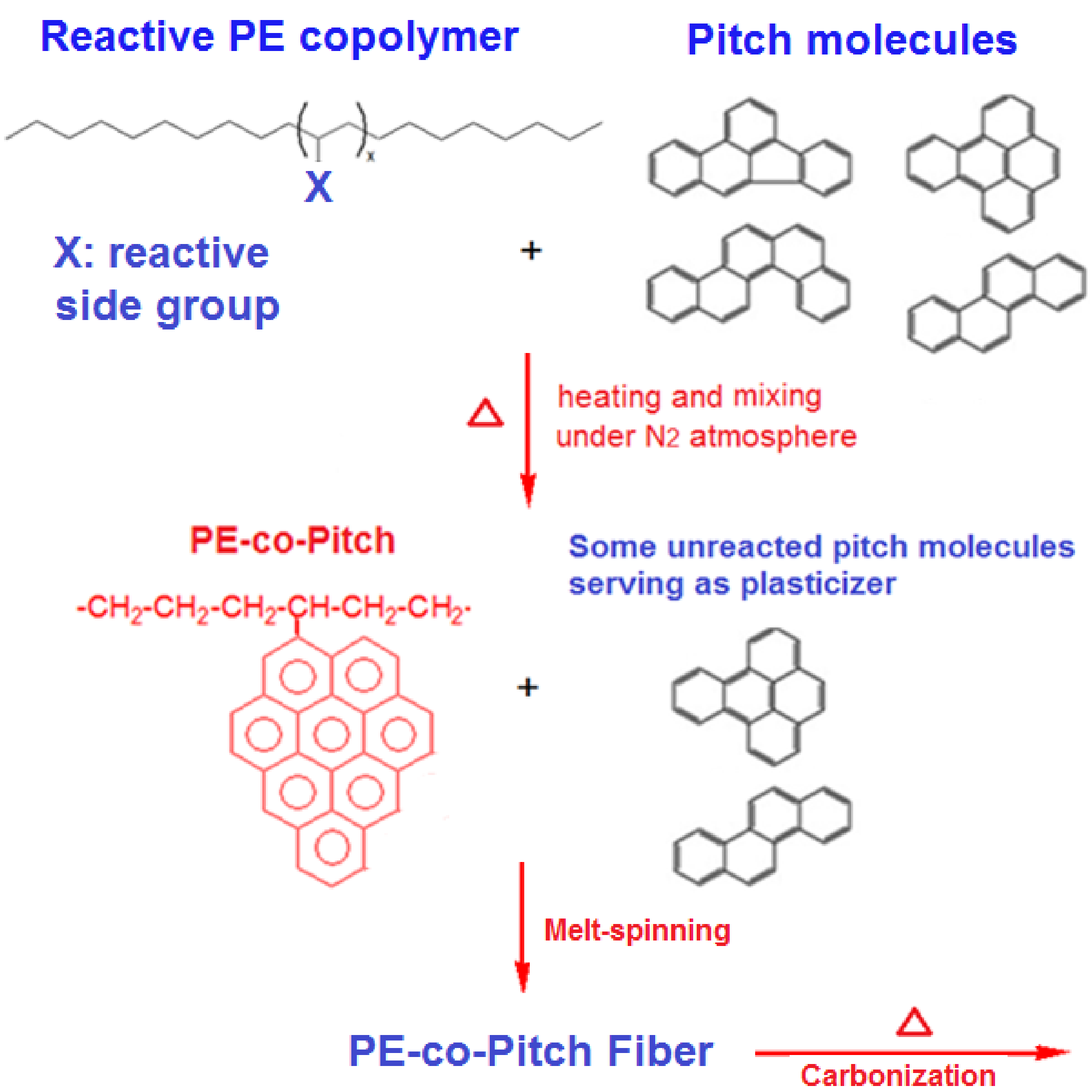
As-Spun | **Carbonized** | **Cross-Section**



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

Future Work: Scope of PE-co-Pitch Precursor

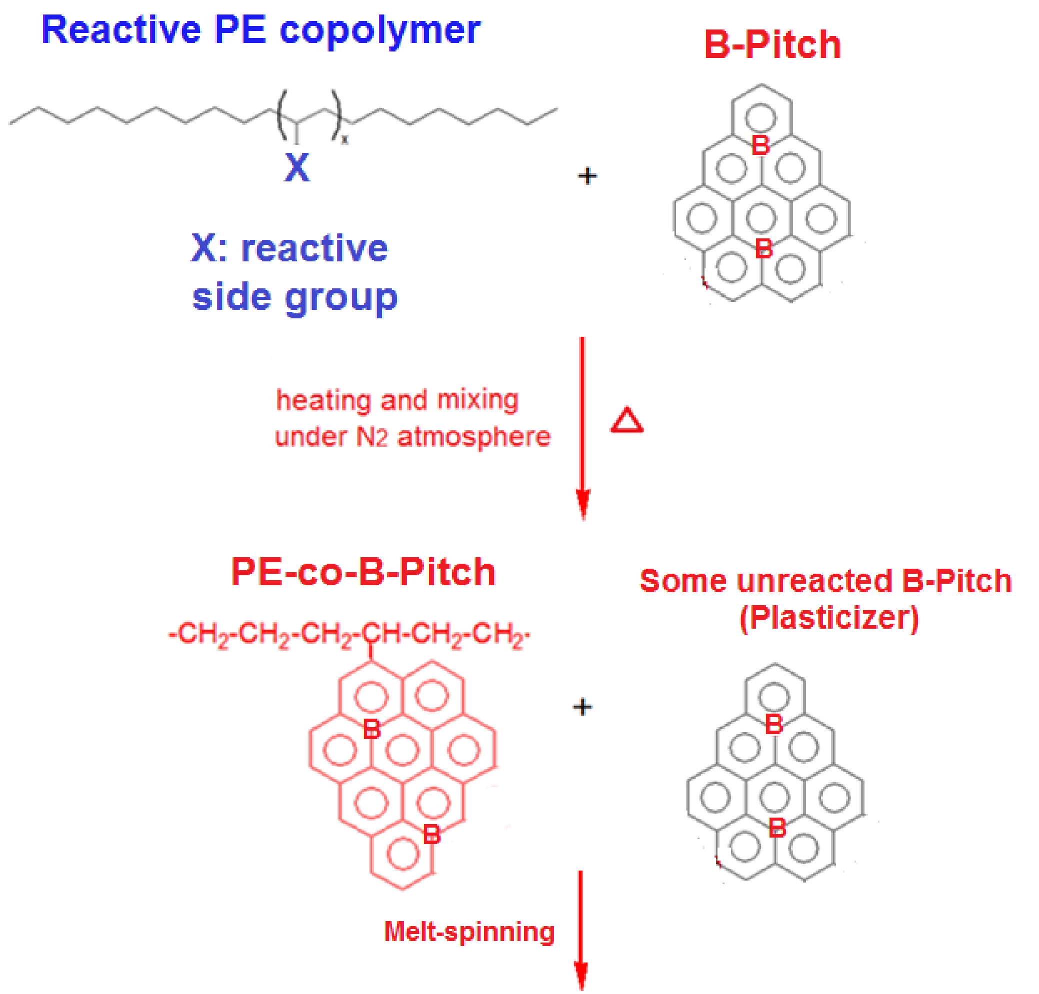


Improve fiber quality:

- PE-X with various reactive group (X) and content
- Pitch material with various composition and reactivity
- Melt-processing condition for PE-co-Pitch precursor
- Melt-spinning with continuous heating and <u>mechanical tension</u>
- Carbonization process under <u>mechanical tension</u> (stretching)

Any proposed future work is subject to change based on funding levels.

Future Work: PE-co-B-Pitch Fiber and B-Carbon Fiber



PE-co-B-Pitch Fiber → (Δ, Carbonization) → B-substituted Carbon Fiber

Melt-spinning on PE-co-B-Pitch:

- **PE-X with various reactive group (X) and content**
- **B-Pitch material with various composition and reactivity**
- **Thermal condition for forming melt-processable PE-co-B-Pitch precursor**
- **Melt-spinning with continuous heating/mechanical tension**
- **Carbonization process under mechanical tension (stretching)**

Any proposed future work is subject to change based on funding levels.

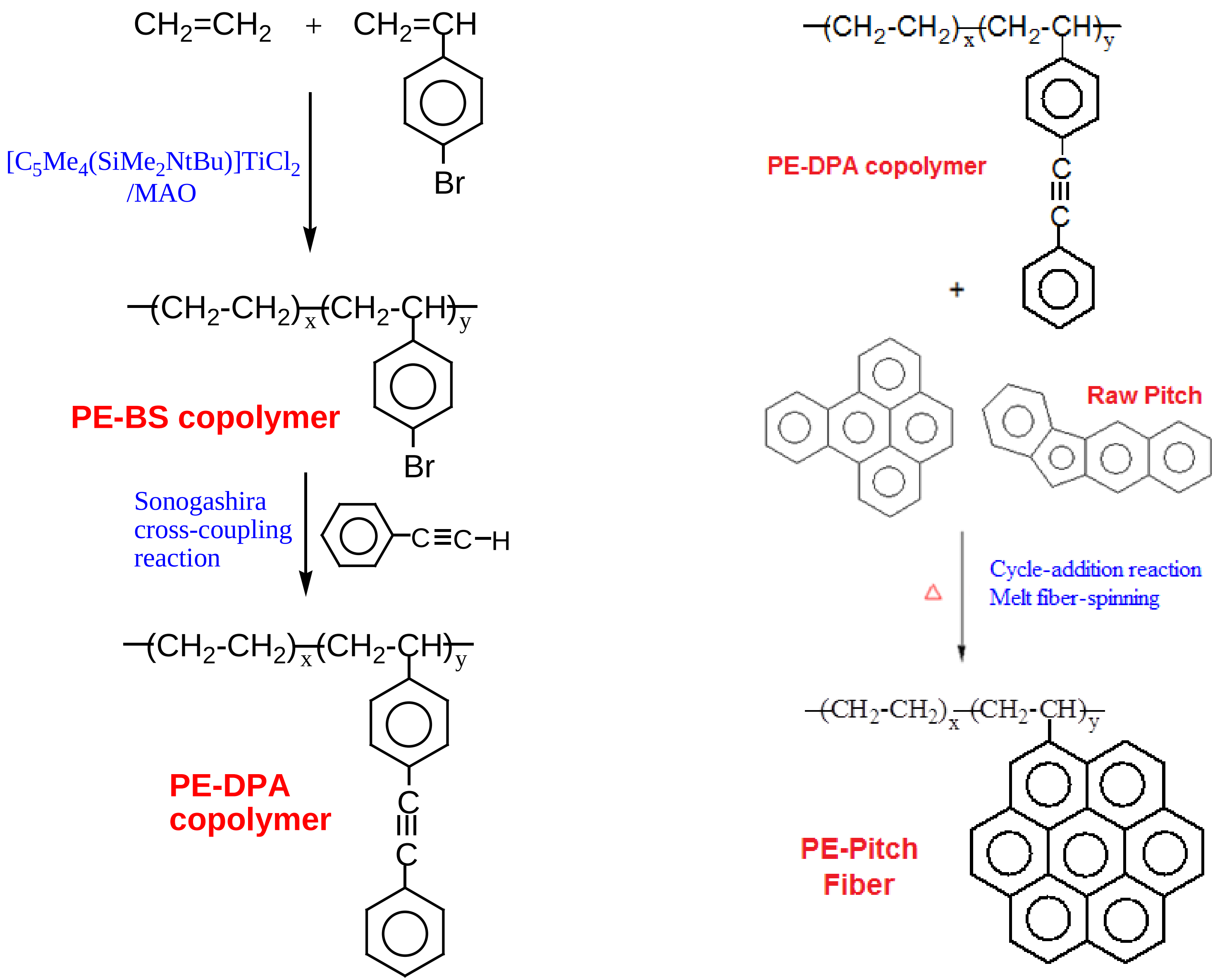
Summary

- A systematical study (design, synthesis, and evaluation) was conducted to identify several new hydrocarbon polymer precursors that can offer >80% carbon yields in *one-step carbonization* under N_2 atmosphere (eliminating the stabilization step in PAN precursor)
- A new class of *low-cost polymer precursors PE-co-Pitch* polymer precursors has also been developed, they are *melt-processible* to form fibers with *high >70% C yields* in *one-step carbonization under* N_2 *atmosphere*
- A new class of B-containing pitch precursors has also been investigated, which shows high conversion yield to B-containing C materials
- Collaborating with ORNL team in fiber processing, thermal conversion, and carbon fiber evaluation.

Collaborations

Partner	Project Roles
Penn State University Dr. Wei Zhu Mr. Houxiang Li Mr. Vandy Sengeh	Design, Synthesis, and Evaluation of New Precursors Fiber-Spinning and Thermal Conversion Carbon Fiber Evaluation
Oak Ridge National Laboratories Dr. Logan Kearney Dr. Amit Naskar	Collaborating with us on Fiber Processing Thermal Conversion Carbon Fiber Evaluation

Synthesis of PE-co-Pitch precursor



<u>*Rheology Study on PE-Pitch Precursor (Pitch 118M)*</u>