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

Project ID: ST147

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University Park, PA 16802

2020 DOE Hydrogen Program Annual Merit Review
May 19-21, 2020

Overview

Timeline

- Project start date: 9/1/2017
- Project end date: 8/31/2020
- % complete: 80%

Budget

- Total project funding: $931,643

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

- Funding for FY2019-20: $308,492
- 1st Go/no-Go decision: Pass in September 2018
- 2nd Go/no-Go decision: Pass in October 2019

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.

Relevance: DOE cost targets

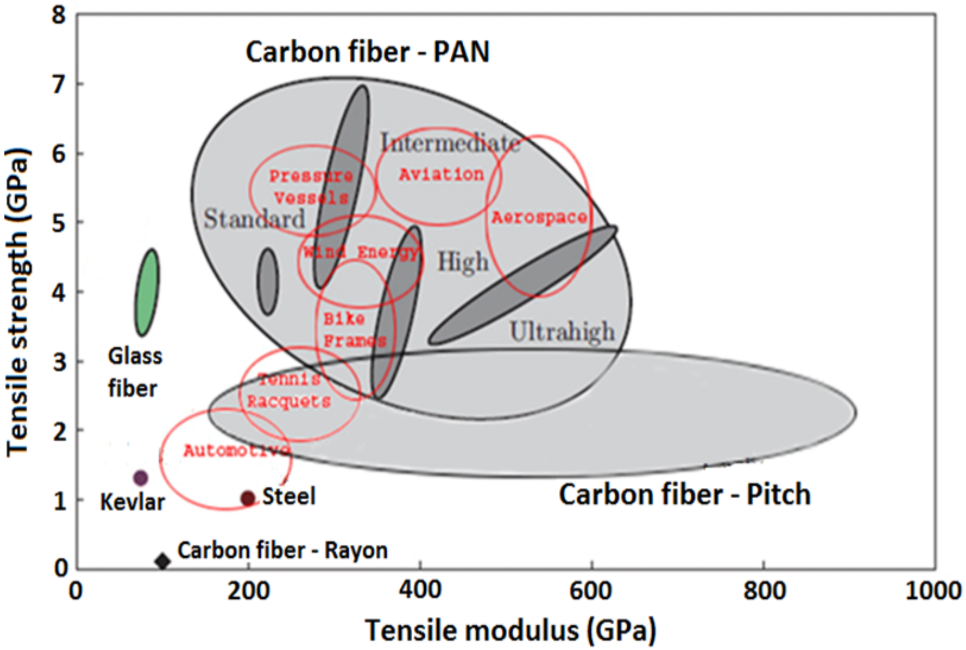
5 gallon tank with 700 bars pressure
5 Kg H_2 storage for 300 miles driving range (45-60 miles/Kg H_2)
High Cost (~ $3,000 per vehicle)

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

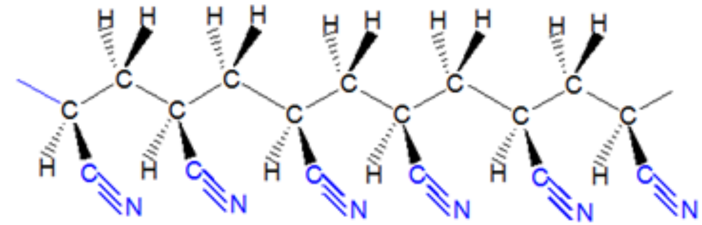
Type IV COPV system with polymer liner and annual production rate of 500,000 systems

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

Relevance: Tensile Properties

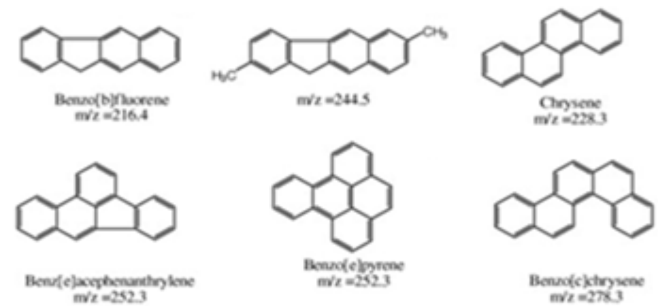


PAN Polymer



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 80%)

Disadvantages:

No applied tension during the conversion

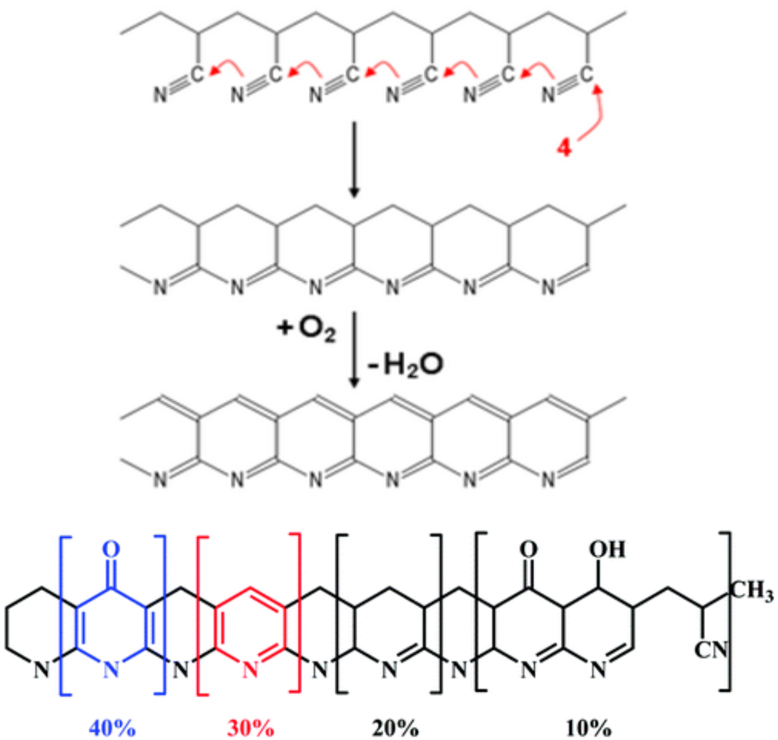
High defects, Poor alignment, Low strength

How to design a precursor with the combined advantages?

Relevance: PAN thermal conversion

Stabilization

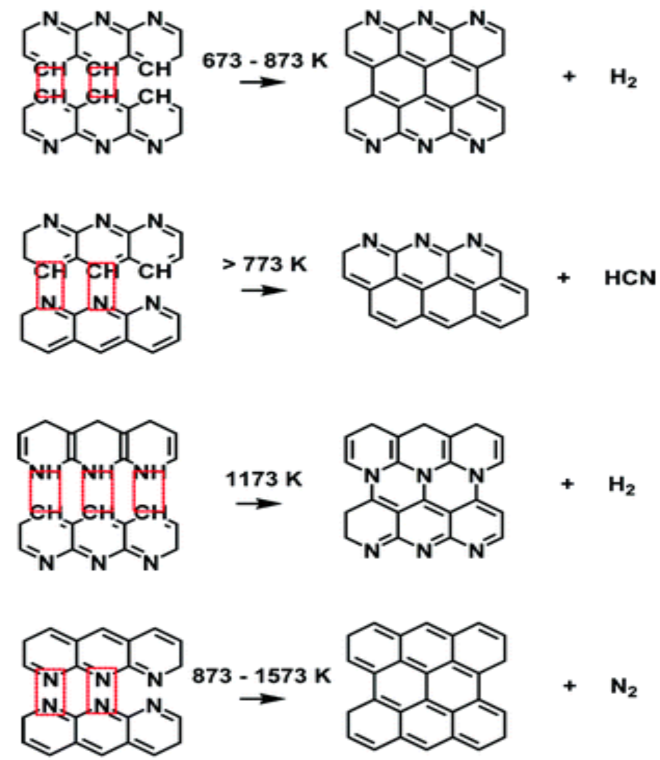
(200-300 ^oC in Air)



(Conjugation, Dehydrogenation, Crosslinking)

Carbonization

(1000-2000 ^oC under N_2)



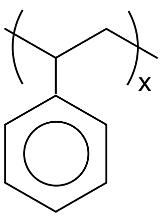
(Hetroatom Removal and Ring-fusion)

PAN offers low C-yield ~50%, due to the combination of inhomogeneous stabilization in core area and drive-off N, O, and H heteroatoms.

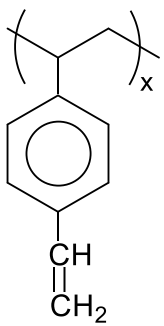
Approach: Design hydrocarbon polymers
(i) high C-yield and (ii) one-step conversion under N_2

Polystyrene (PS) backbone

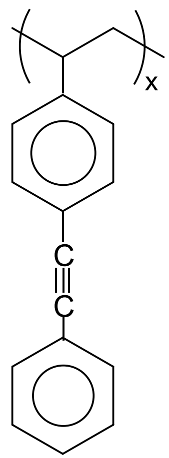
PS



PS-V

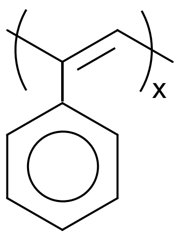


PS-PA

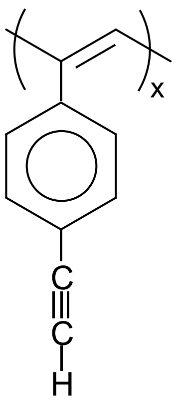


Poly(phenylacetylene) (PPA) backbone

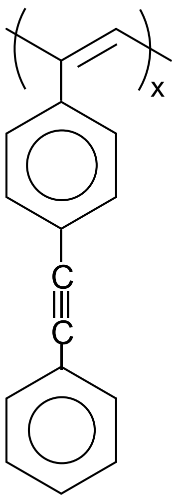
PPA



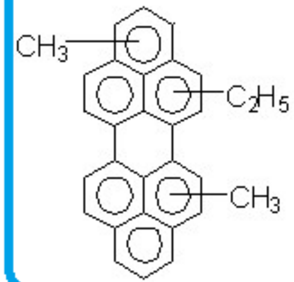
PPA-A



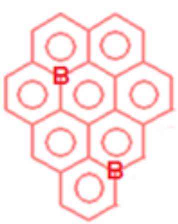
PPA-PA



Pitch



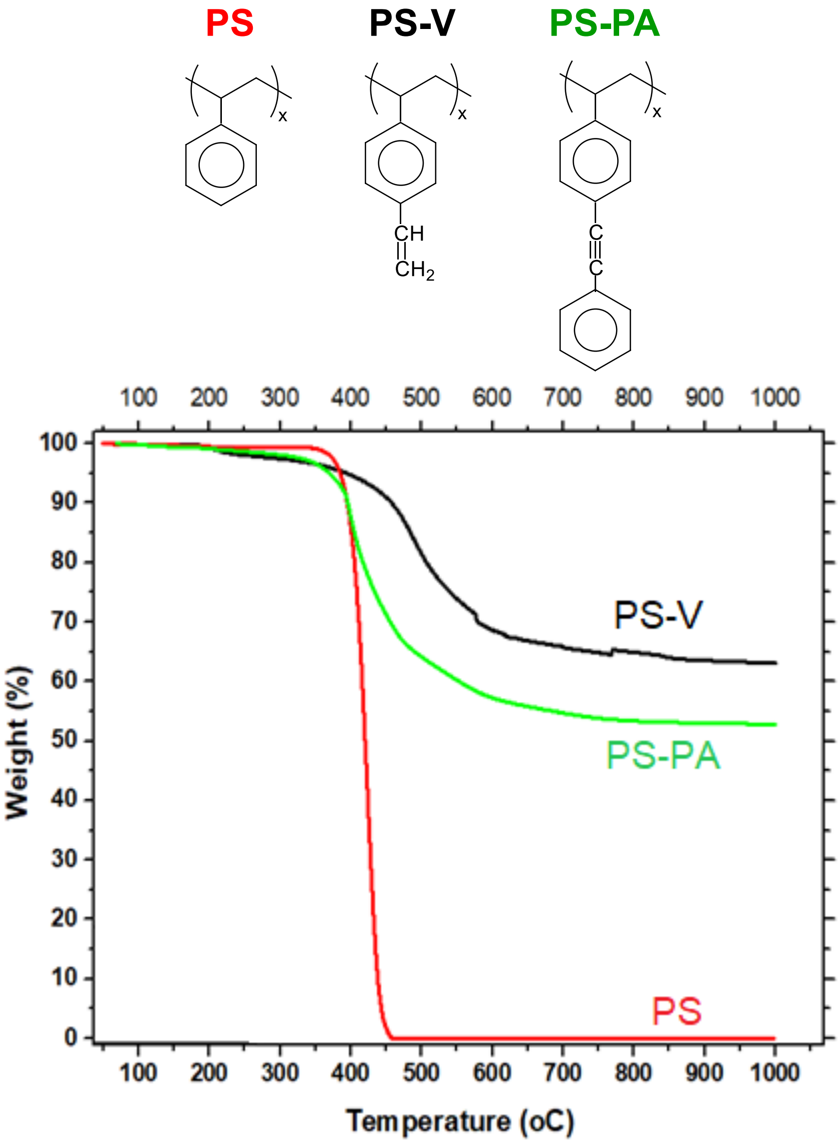
B-Pitch

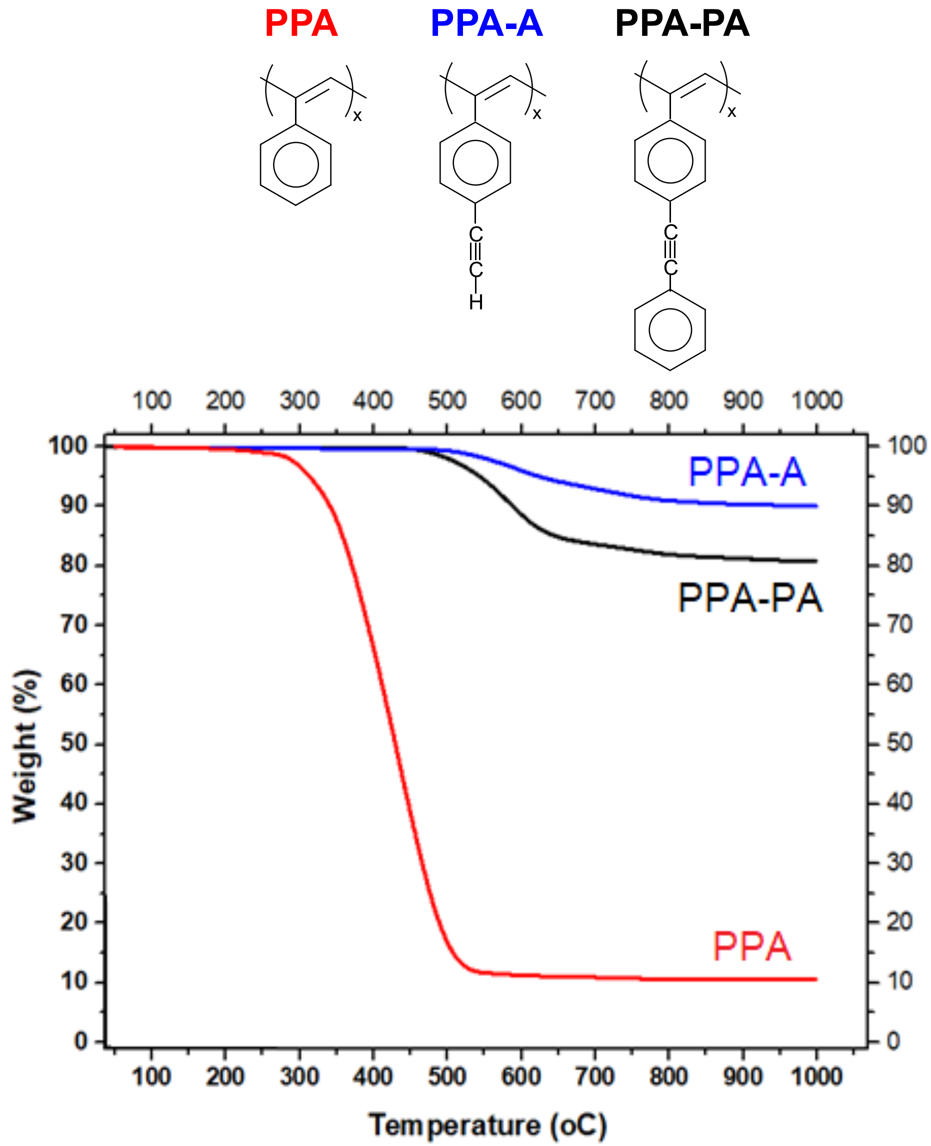


Thermal-induced stabilization reactions without O_2:

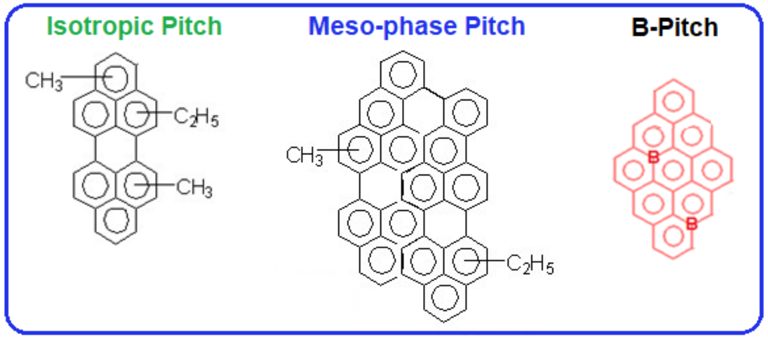
- **Dehydrogenation reaction**
- **π-Electrons conjugation**
- **Crosslinking reaction**

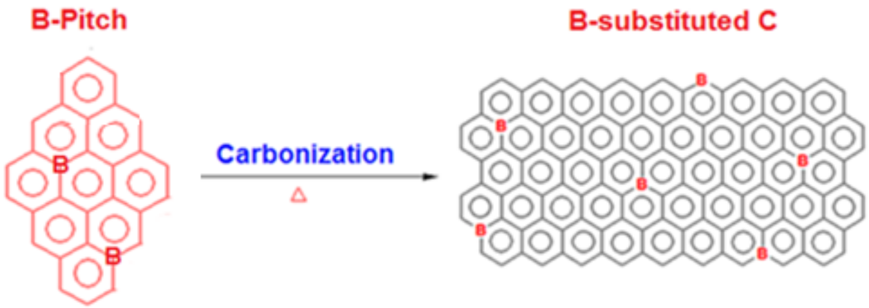
Accomplishments: C-yields of polymer structures (one-step thermal conversion under N_2)

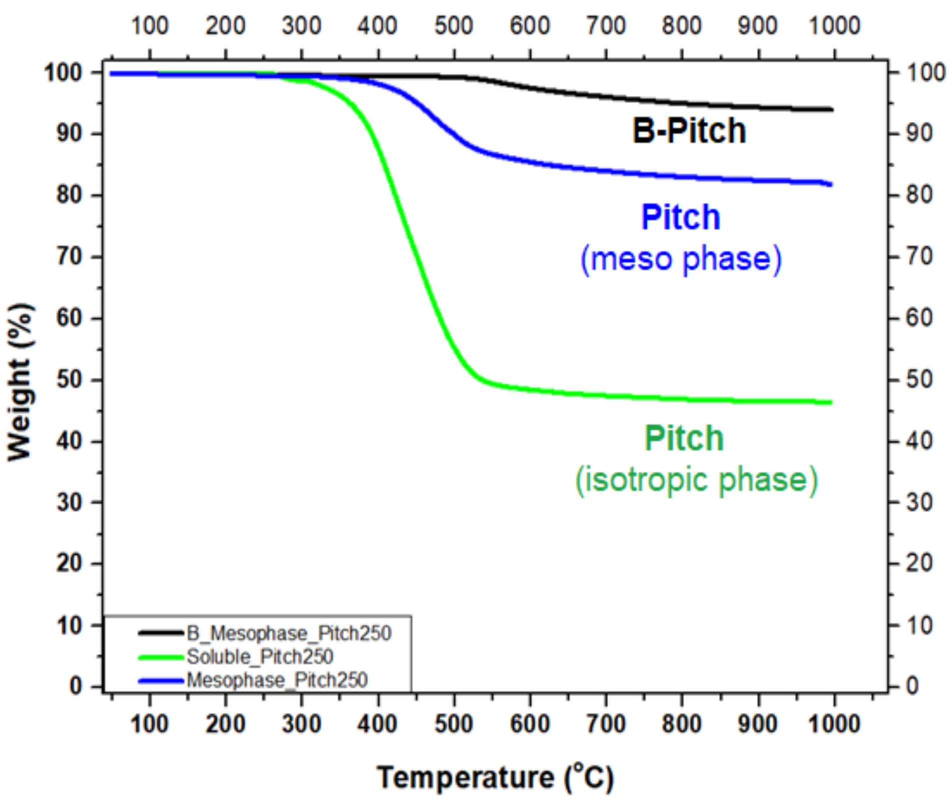




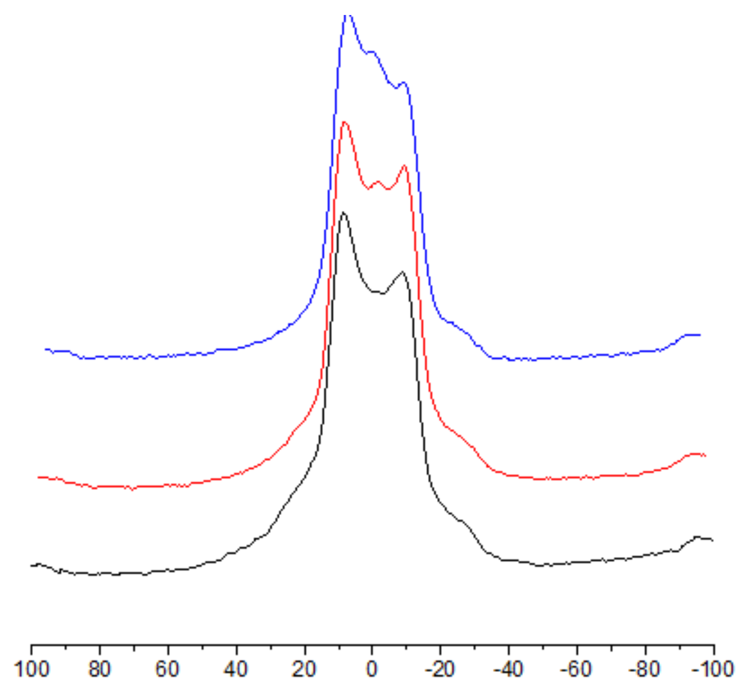
Accomplishments: C-yields of pitch structures (PAH) (one-step thermal conversion under N_2)





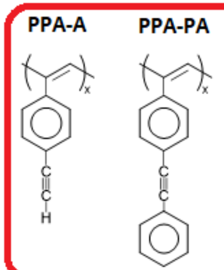


[11]B NMR of several B/C materials



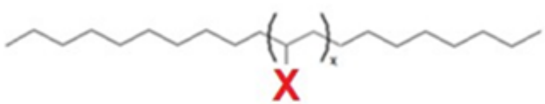
Approach: Design new PE-g-Pitch precursors

with (i) high C-yield under N_2, (ii) melt processible, and (iii) low-cost



Both PPA-A and PPA-PA precursor polymers with high C-yields are solution-processible, but not melt-processible. They start the stabilization reactions before their softing temperature. They are also not low-cost precursors.

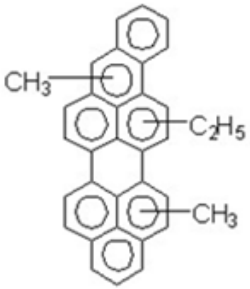
Reactive PE copolymer



X: few mol% of reactive sites

\+

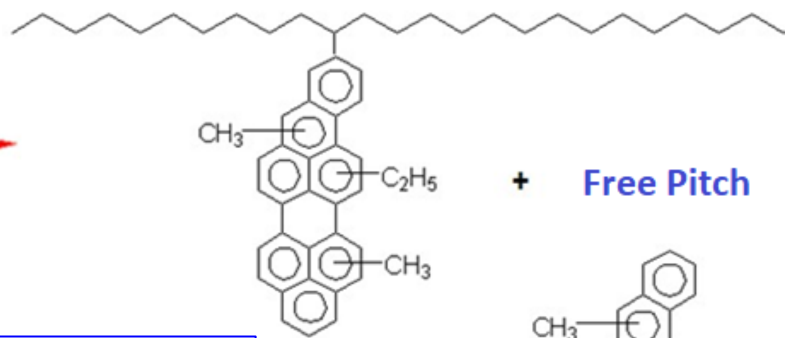
Pitch (PAH) molecules



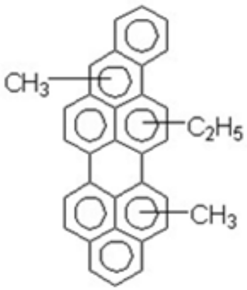
melt-mixing in extruder

△ < 320 °C, under N_2

PE-g-Pitch polymer



\+ Free Pitch



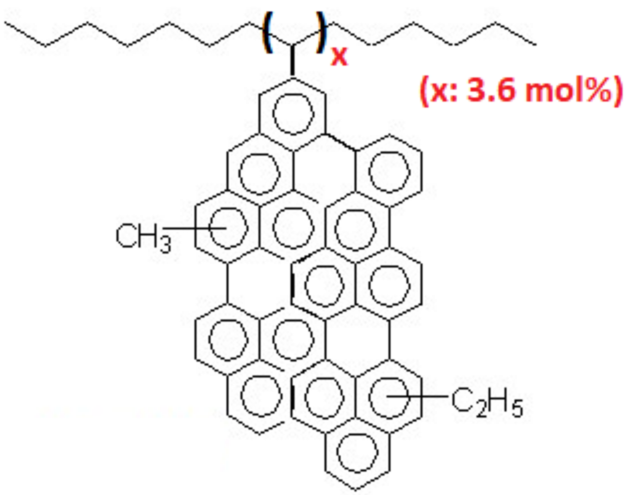
Requirements of X Reactive Group:

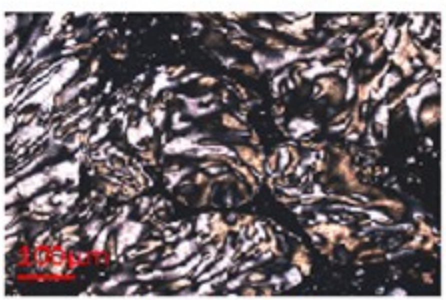
- A complete and selective coupling reaction between X and PAH groups.
- No any residue X groups and no X-X coupling.

PE-g-Pitch shall be stable and melt-processible at <350 °C (Pitch reaction temperature)

Accomplishment: PE-g-Pitch (I) (mesophase precursor)

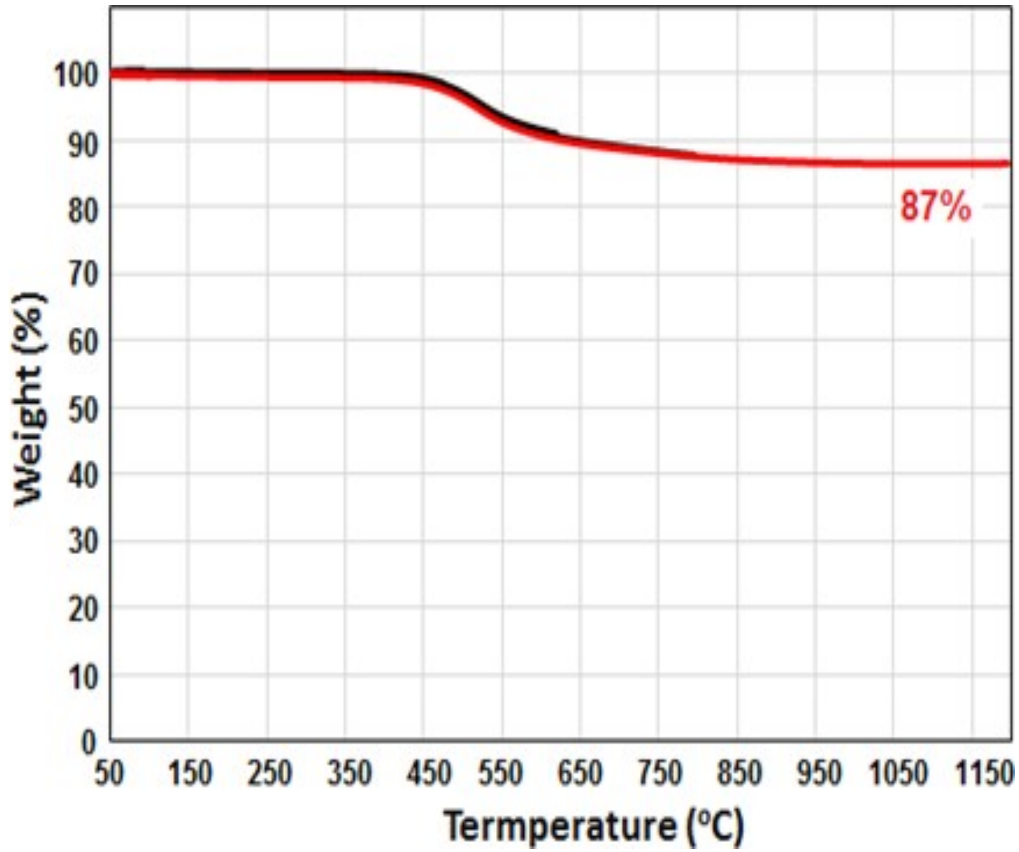
PE-g-Pitch polymer (I)





Mesophase

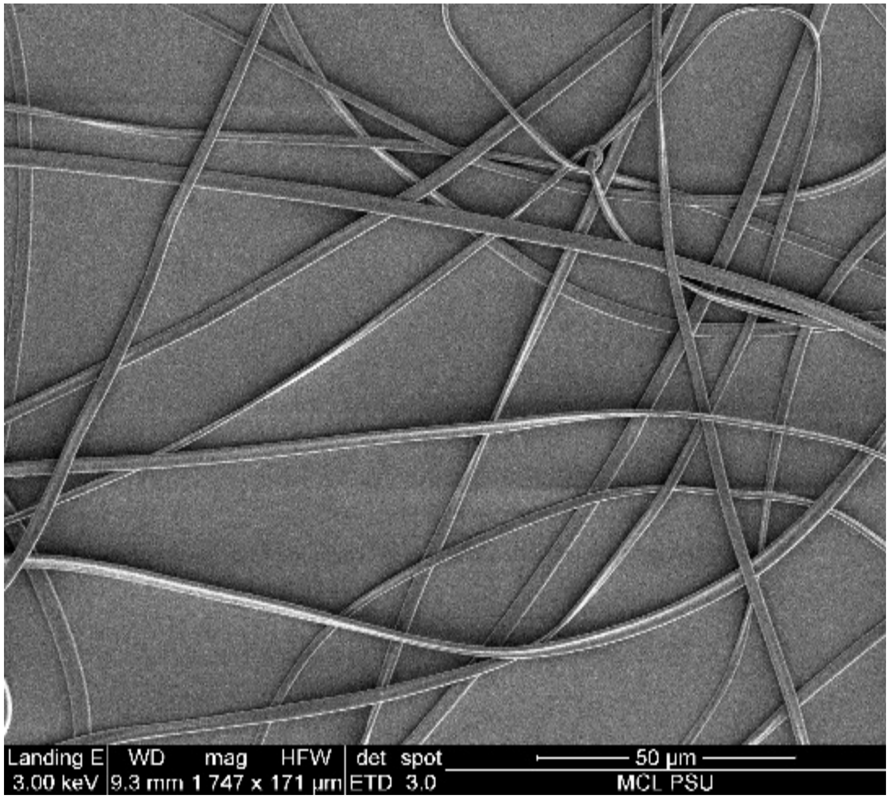
TGA curve under N_2

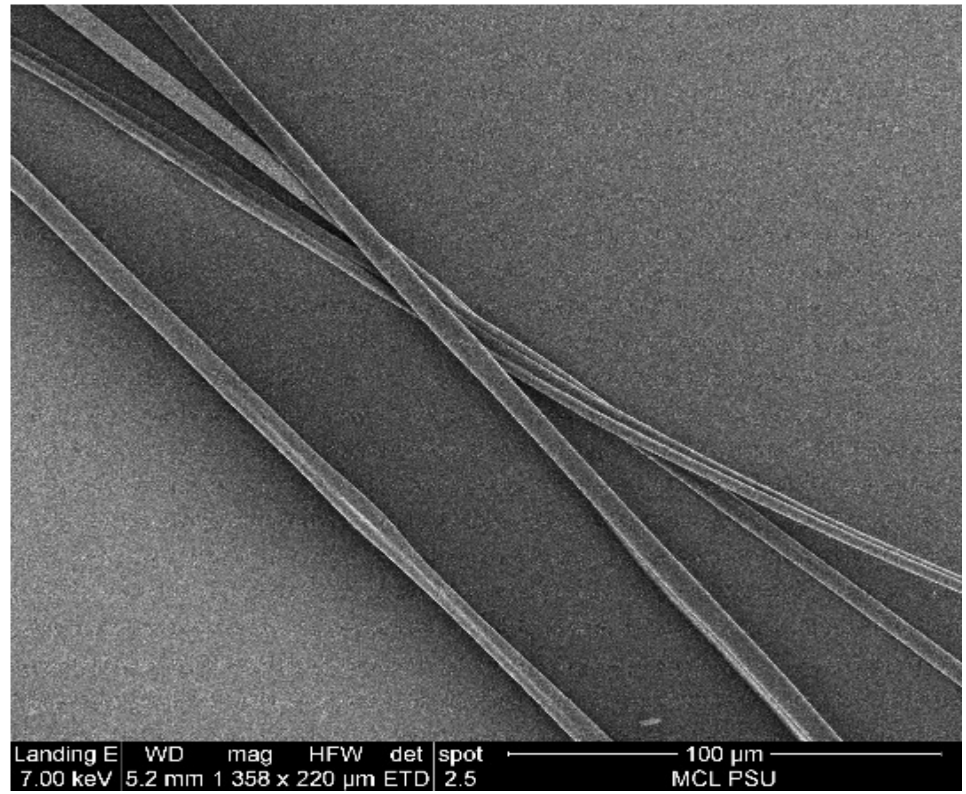


One step C conversion under N_2 atmosphere with high C-yield (87%)

The resulting mesophase PE-g-Pitch precursor shows high melt-viscosity

Accomplishments: SEM micrographs of electrospun Mesophase PE-g-Pitch (I) fibers

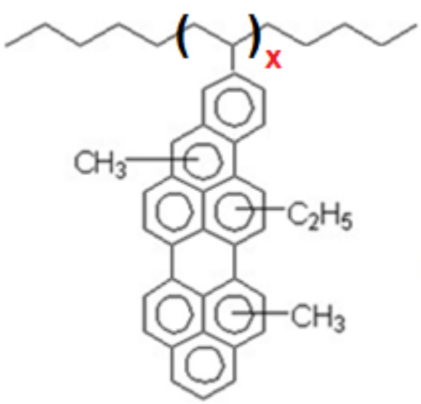




Dry-spinning from 30 wt% polymer solution in toluene solvent

Accomplishments: PE-g-Pitch (I) (isotropic Pitch)

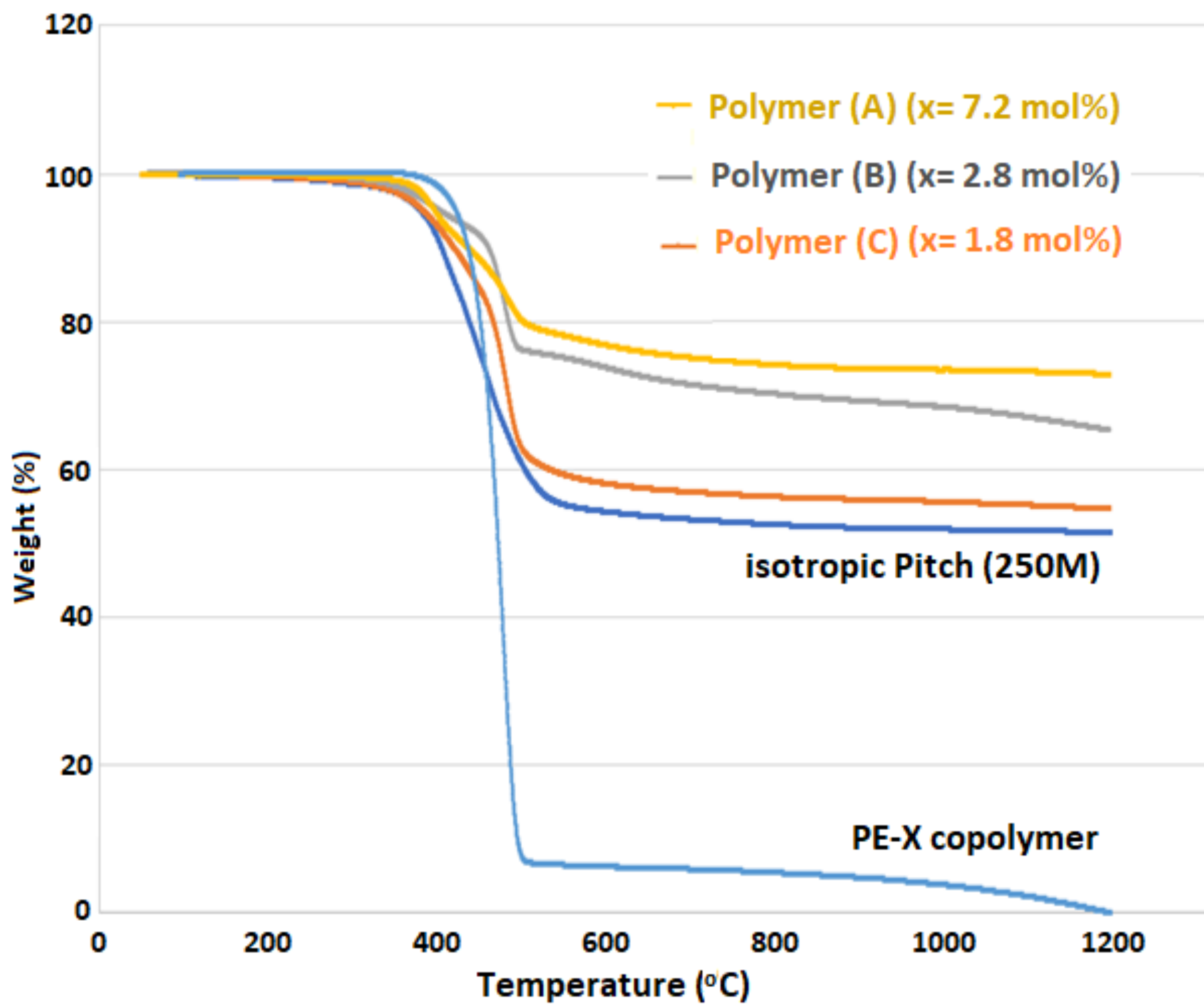
PE-g-Pitch (I)
(isotropic)



Polymer (A): x=7.2 mol%

Polymer (B): x=2.8 mol%

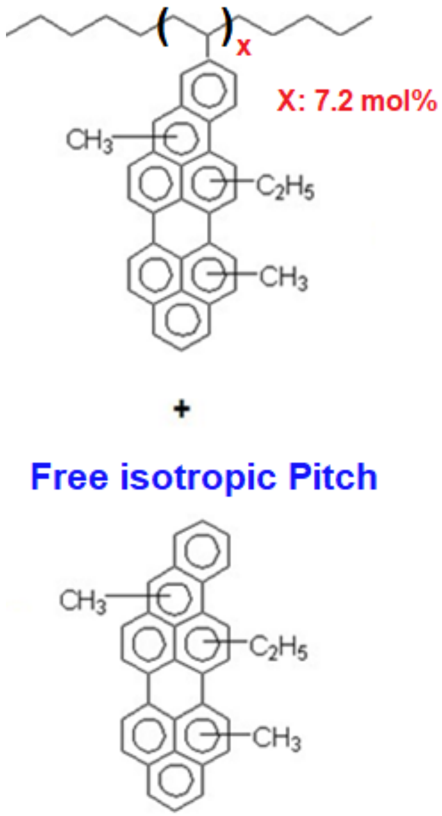
Polymer (C): x=1.8 mol%



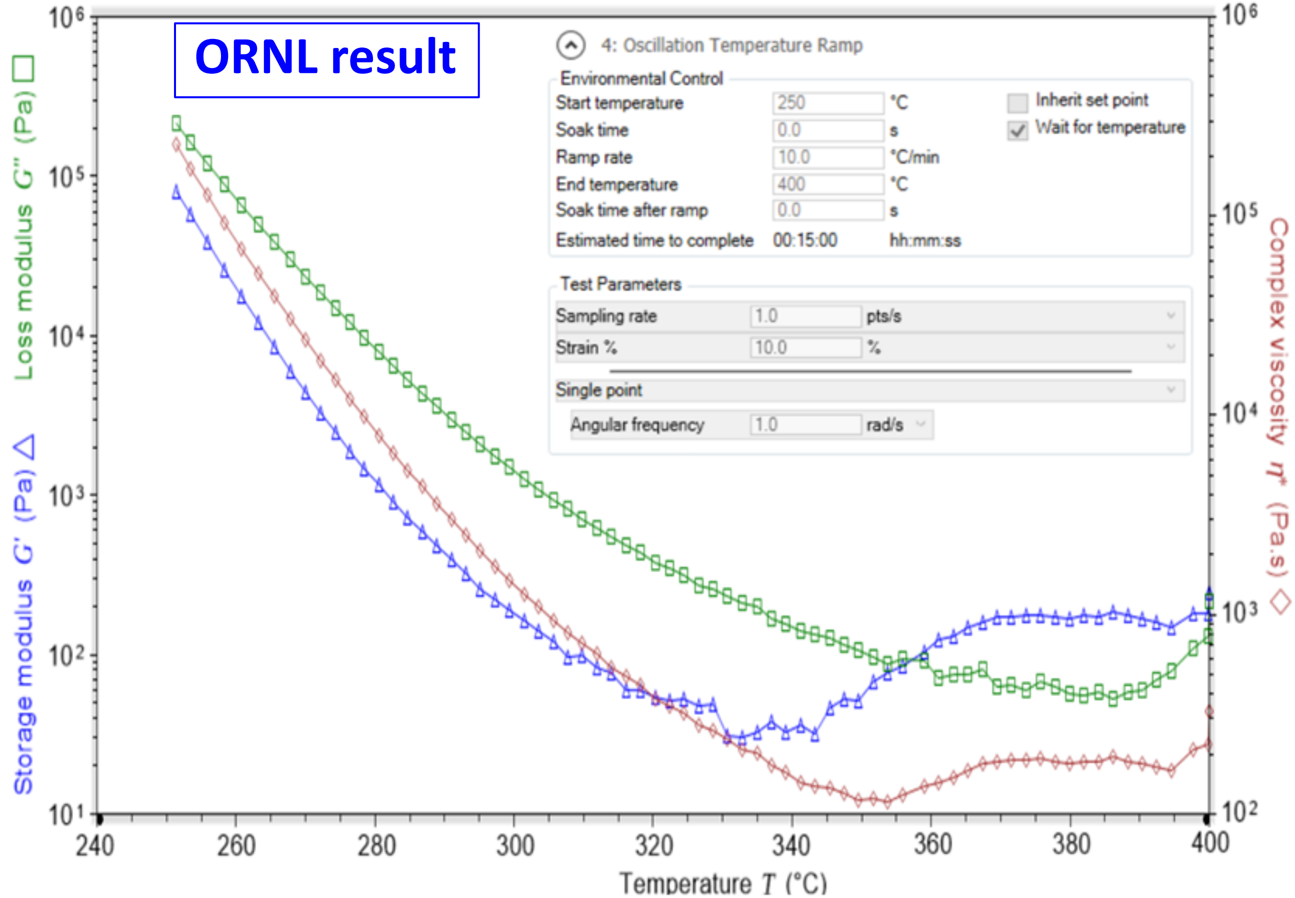
All PE-g-Pitch (I) precursors show higher C yield than both PE-X and Pitch.

Accomplishments: Melt-processible PE-g-Pitch (I)/Pitch

PE-g-Pitch (I) (isotropic)

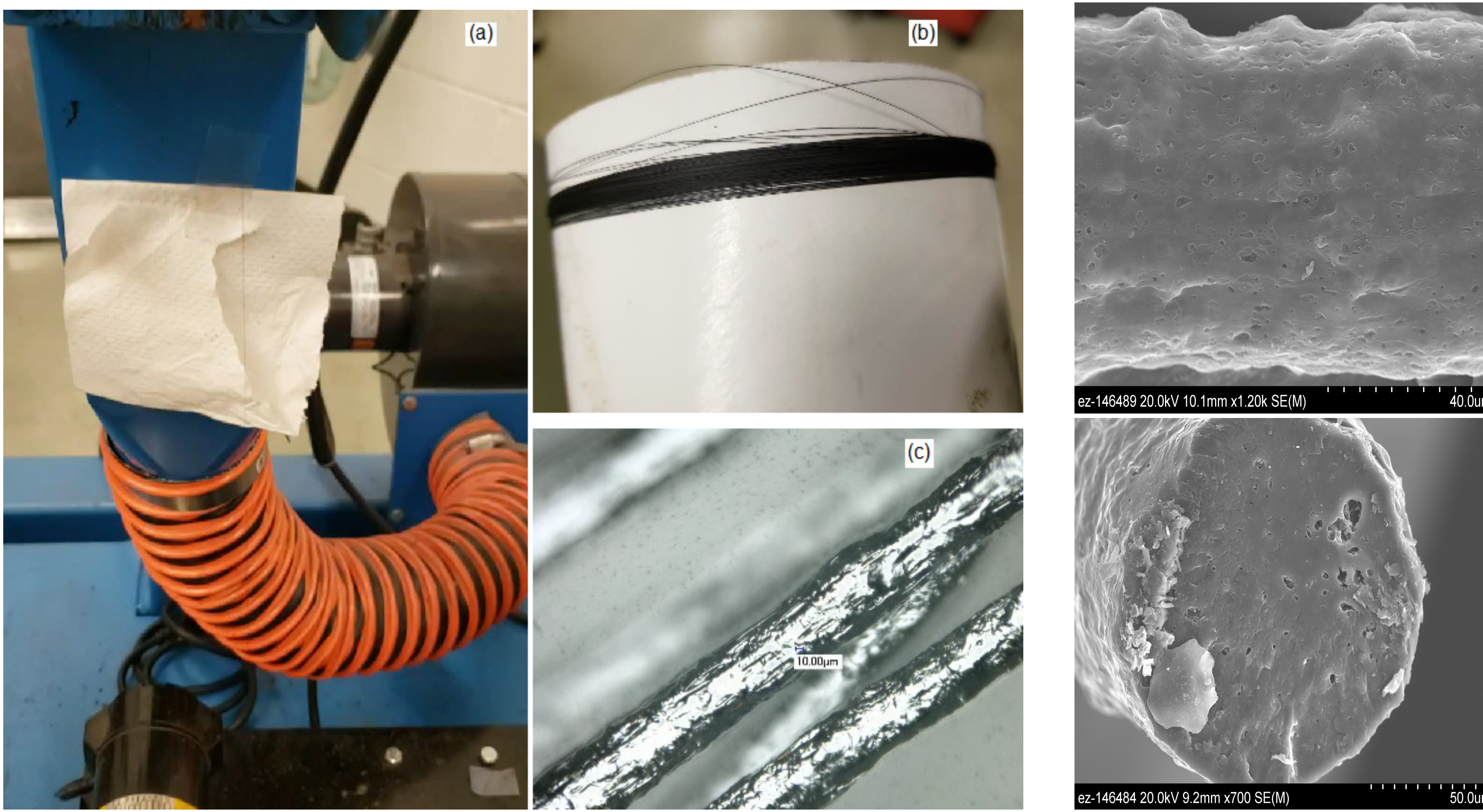


Oscillation Rheology (temperature sweep)



- **The suitable melt-processing temperature <330 ^{o}C**
- **This PE-g-Pitch (I) precursor was scaled up to >100g for the melt-spinning at ORNL**

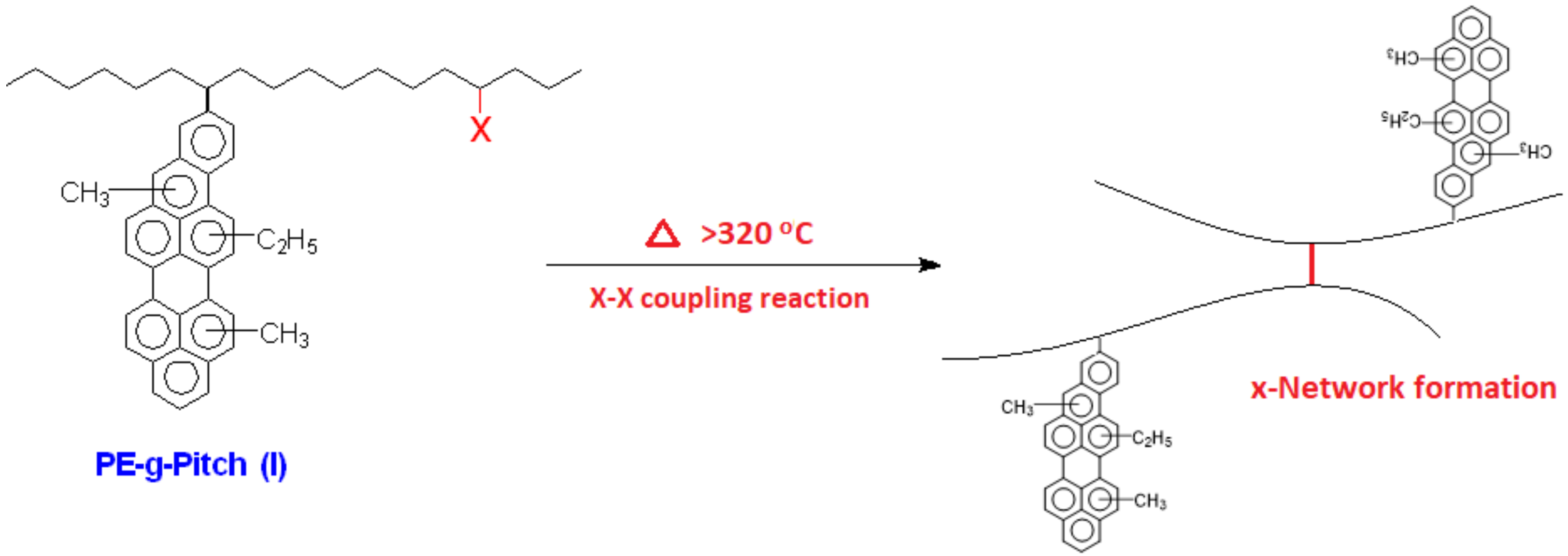
Accomplishments: Melt-spun PE-g-Pitch fibers at ORNL



- ***PE-g-Pitch precursor was spun continuously using ORNL laboratory-scale single-filament spinning apparatus in the temp. range of 320-360 ^{o}C.***
- ***The fiber shows somewhat uneven surfaces and many small voids.***

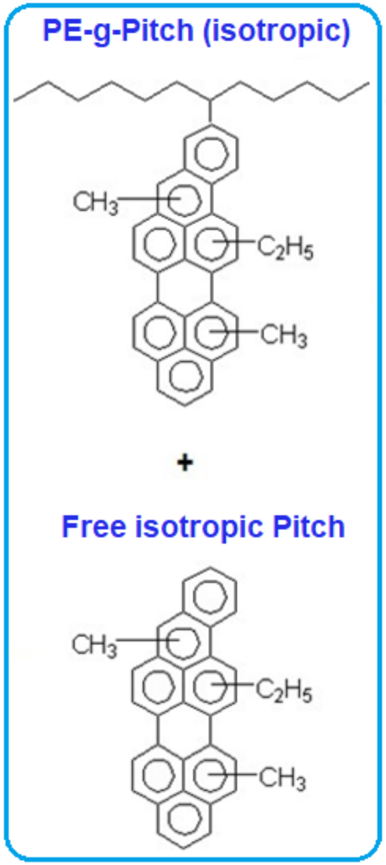
Accomplishments: PE-g-Pitch (I) precursor

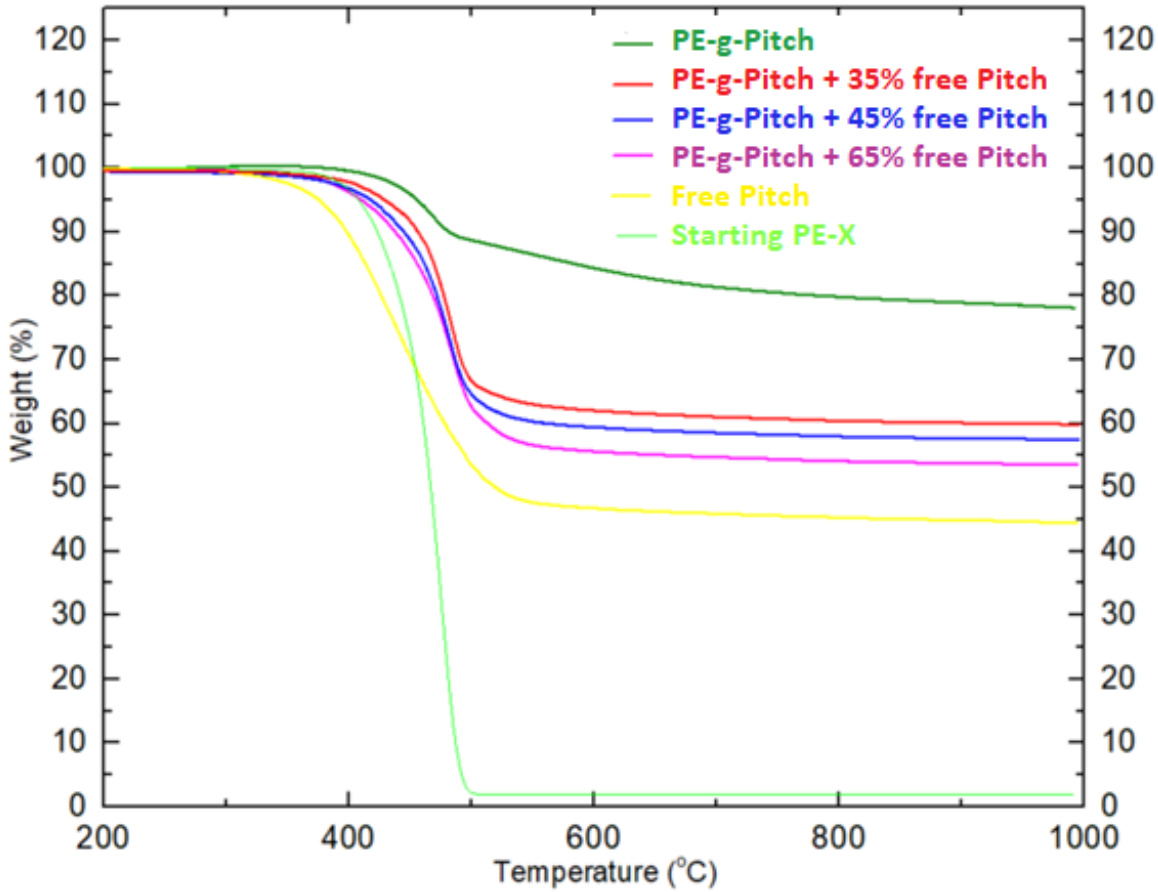
- PE-g-Pitch (I) polymer (with meso-phase pitch) shows >85% C-yield and uniform fibers by solution-spinning, but not melt-processible.
- PE-g-Pitch (I) polymer (with isotropic pitch) shows >70% C-yield and is melt-processible with some free Pitch (Plasticizer). However, it is difficult to prepare uniform fiber due to instability of polymer at >330 °C (melt-processing temp.).



Require the PE-X copolymer with reactive X groups that can achieve completely and selectively coupling reaction with PAH molecules. (No residue X groups and no X-X coupling reaction)

Accomplishments: New PE-g-Pitch precursor (II)

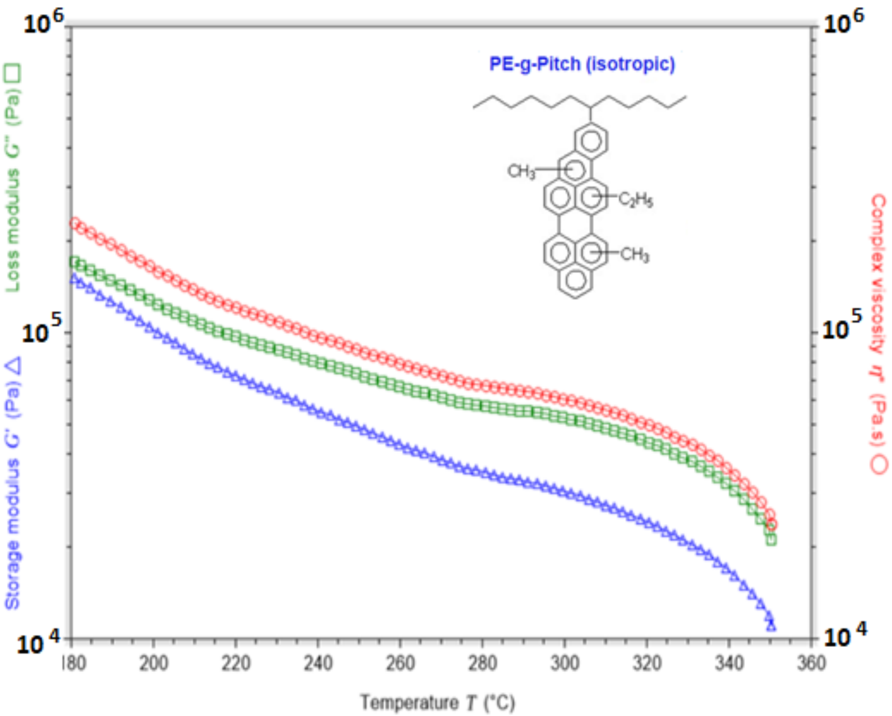


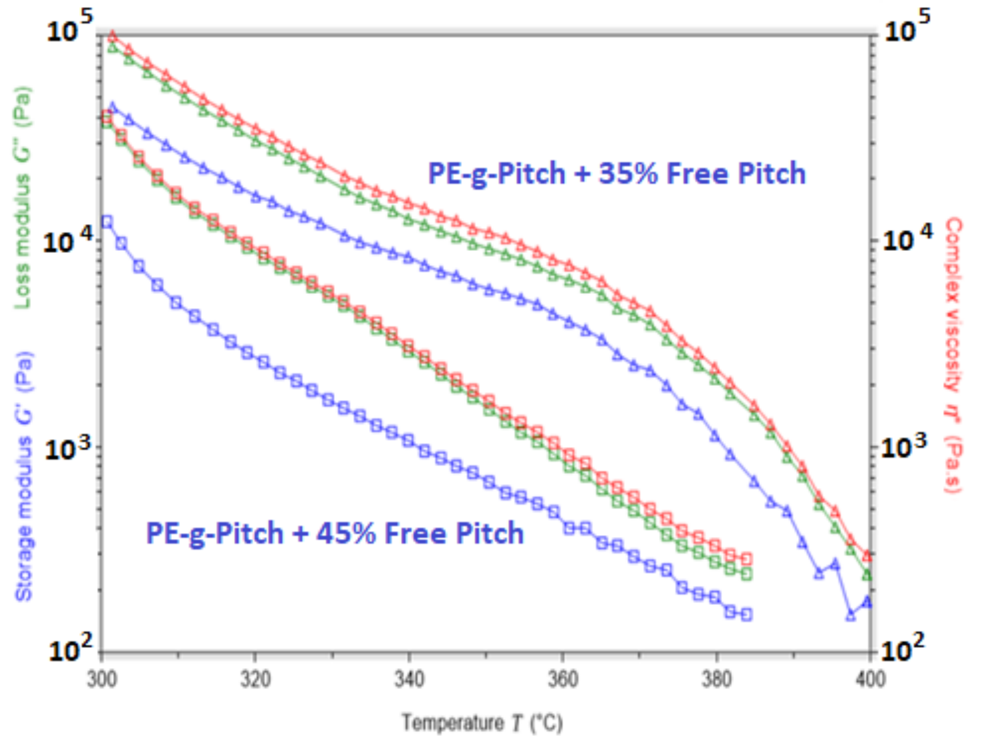


Sample	PE-g-Pitch	PE-g-Pitch with 35% free Pitch	PE-g-Pitch with 45% free Pitch	PE-g-Pitch with 65% free Pitch	Free Isotropic Pitch	Starting Reactive PE-X
C-Yield	78.4	60.1	57.6	53.2	49.4	2.1

Accomplishments: Melt-processible PE-g-Pitch precursor (II)

Oscillation Rheology (temperature sweep)



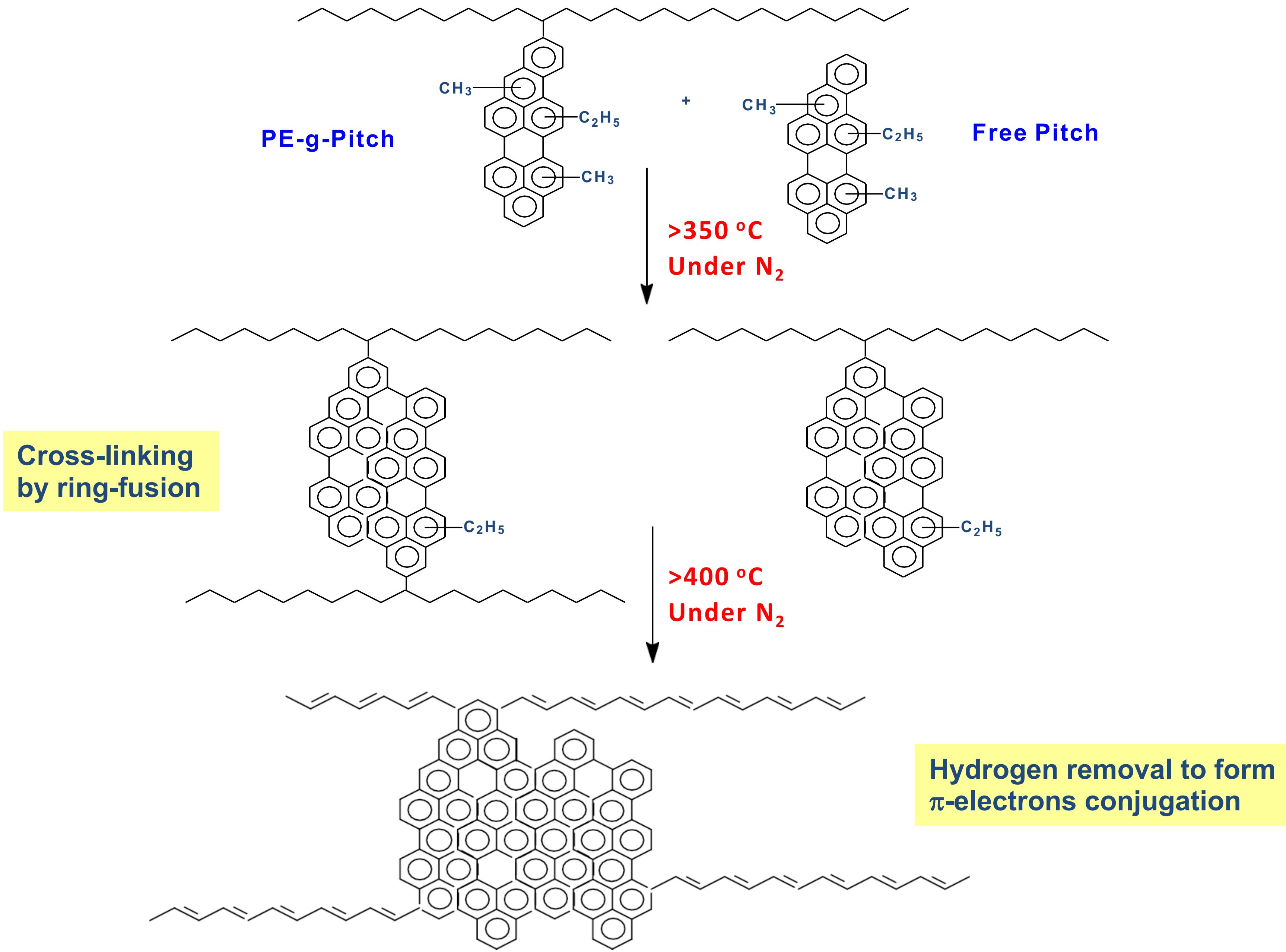


Sample	C-Yield
PE-g-Pitch	78.4
PE-g-Pitch + 35% Pitch	60.1
PE-g-Pitch + 45% Pitch	57.6

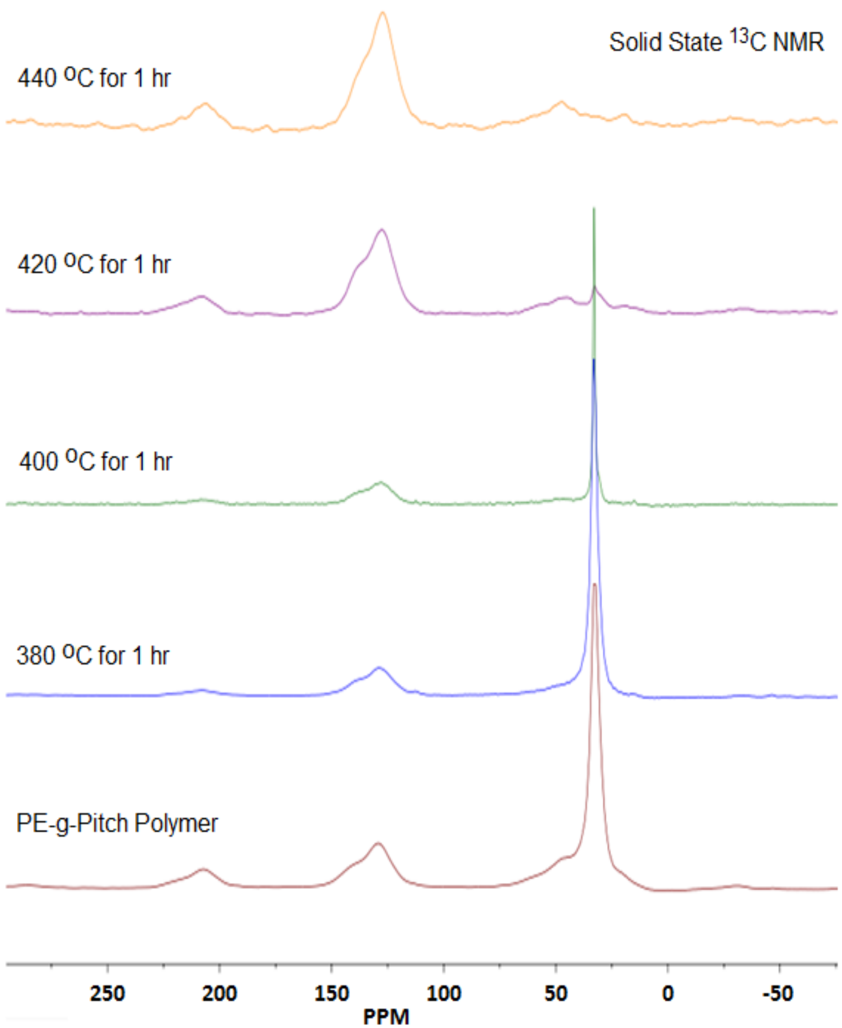
The most suitable precursor composition: PE-g-Pitch with 45% free Pitch.

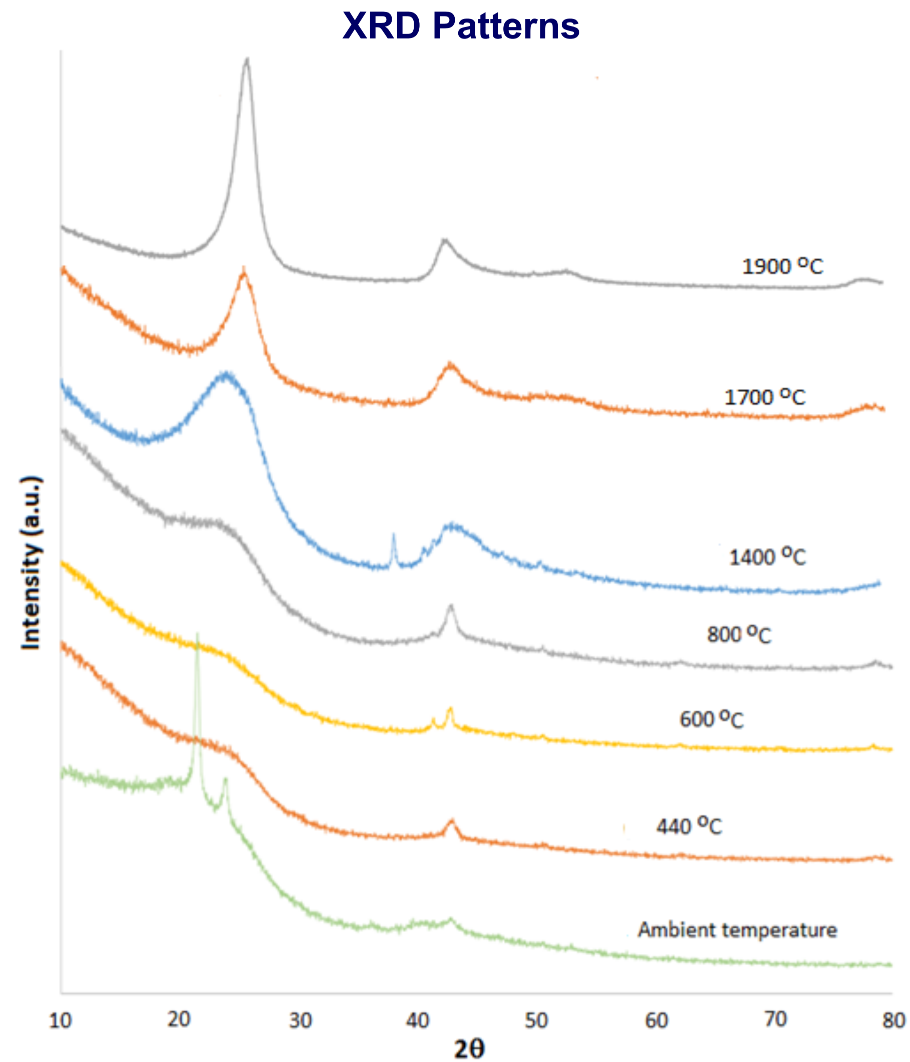
The most suitable melt-spinning temp: 320-340 °C.

Accomplishment: Stabilization Mechanism of PE-g-Pitch Precursor



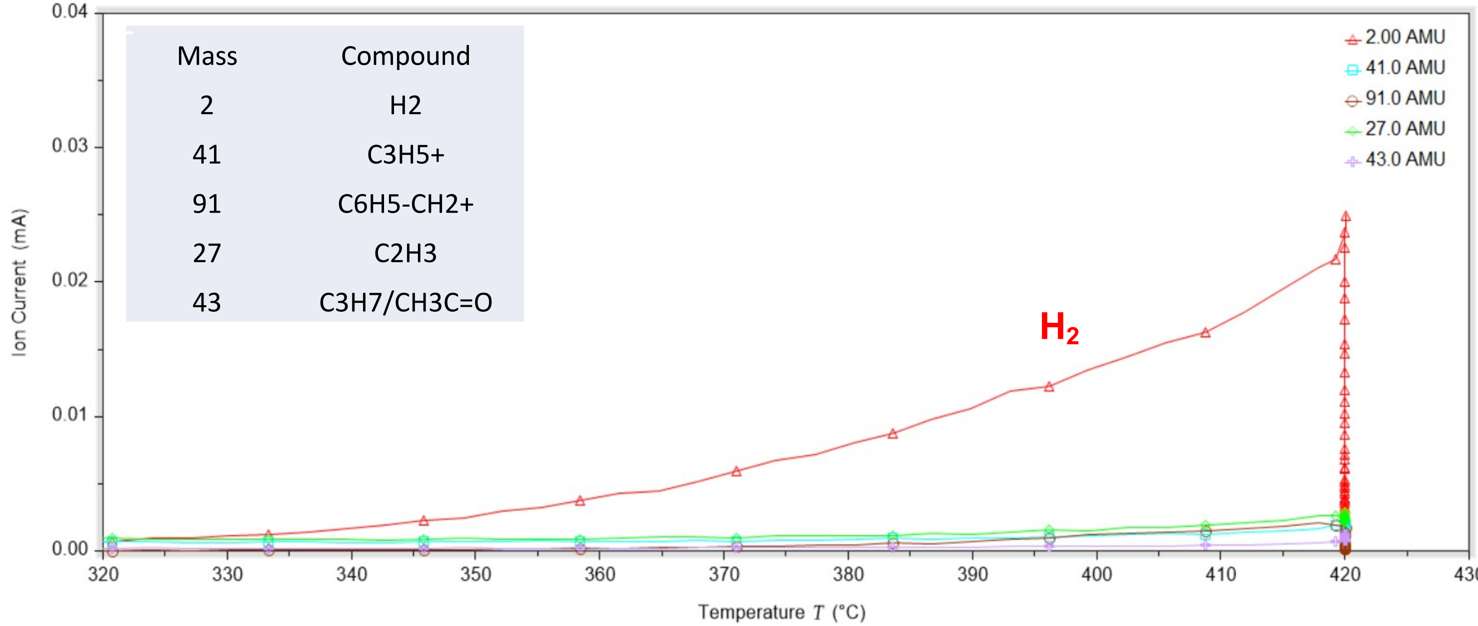
Accomplishments: ^{13}C NMR and XRD spectra of PE-g-Pitch fiber during thermal conversion to CFs under N_2

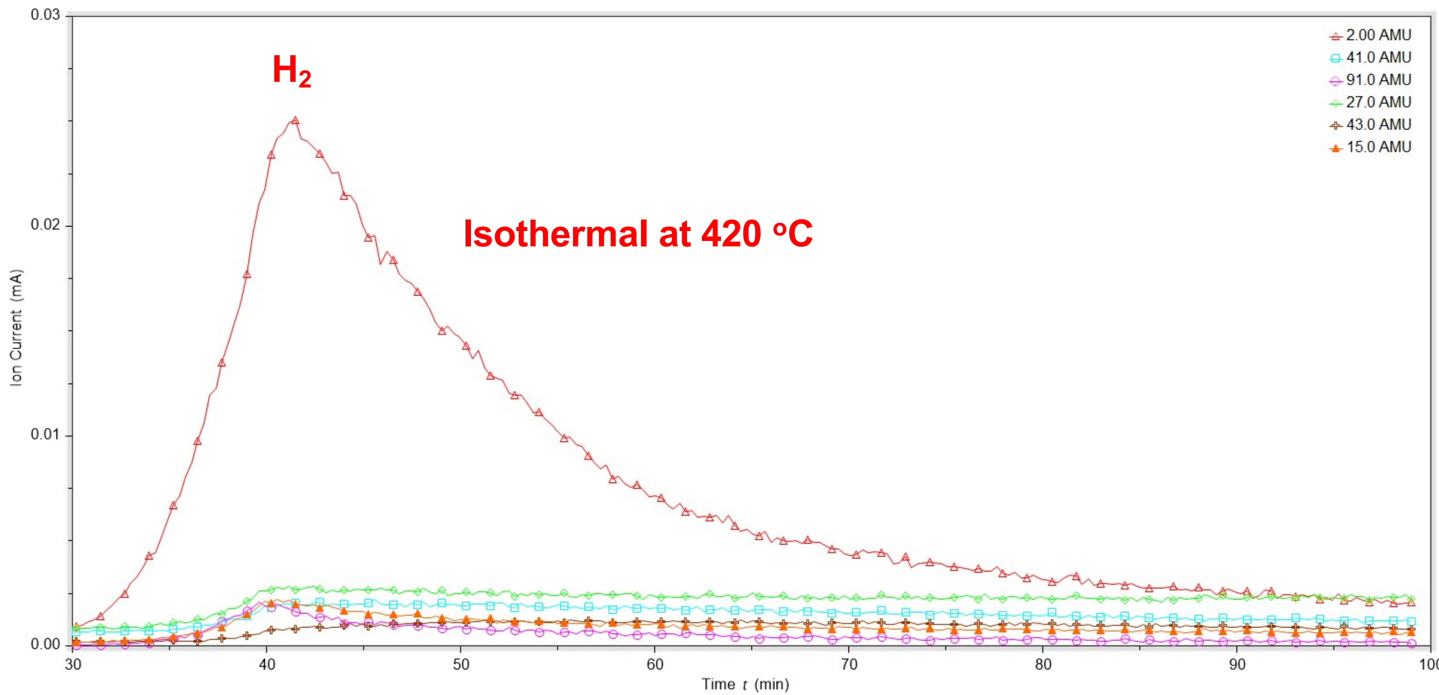




PE polymer chain is conversed to aromatic structure at 400-440 °C under N_2

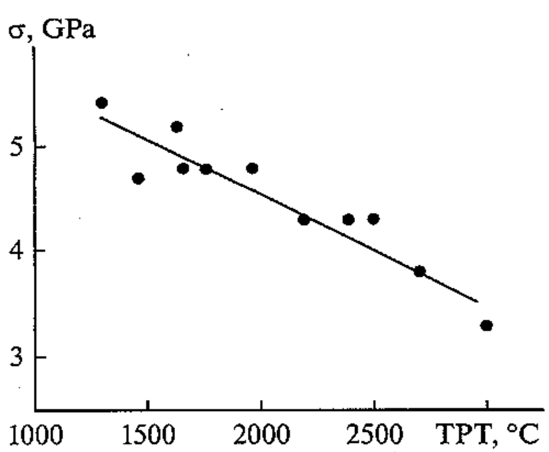
Accomplishment: TGA-Mass Results during Stabilization

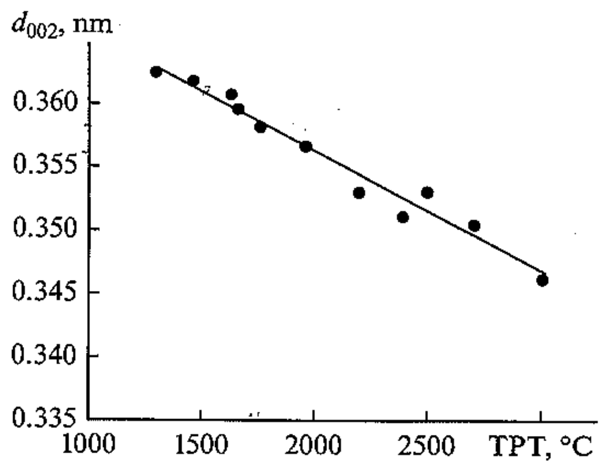


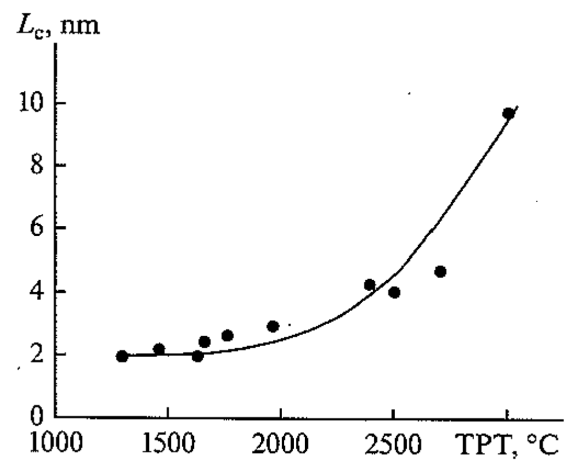


Accomplishments: XRD comparison of Carbon Fibers

	PE-g-Pitch based Carbon Fiber			PAN-based Carbon Fibers*	
Temperature (°C)	D_{002} interlayer spacing (nm)	Lc (nm)	La (nm)	D_{002} interlayer spacing (nm)	Lc (nm)
1500 (Sample 1)	0.3674	1.5774	5.1327	0.361	2.0
1700 (Sample 1)	0.3500	2.5778	6.2958	0.357	2.5
1900 (Sample 1)	0.3480	3.2731	7.4849	0.351	3.1
1400 (Sample 4)	0.3708	1.2968	4.6150	0.364	2.0
1700 (Sample 4)	0.3549	1.6697	5.9562	0.357	2.5
1900 (Sample 4)	0.3524	3.9405	6.9944	0.351	3.1





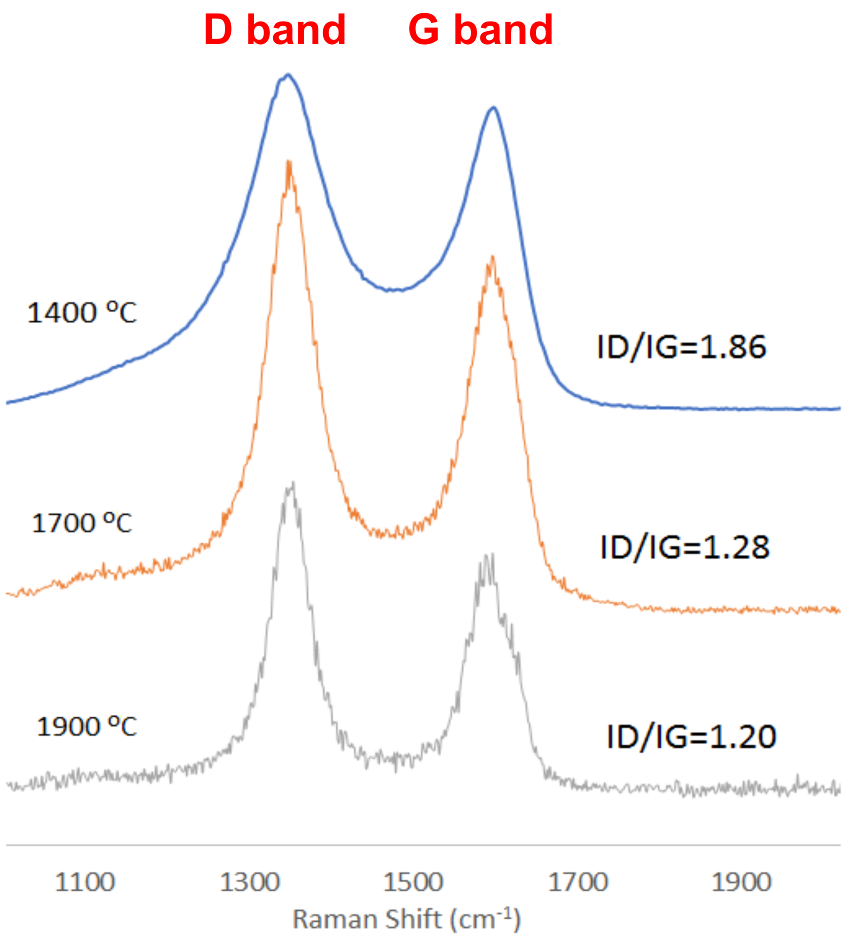


* Inorganic Materials: Applied Research **2018**, 9, 890-899

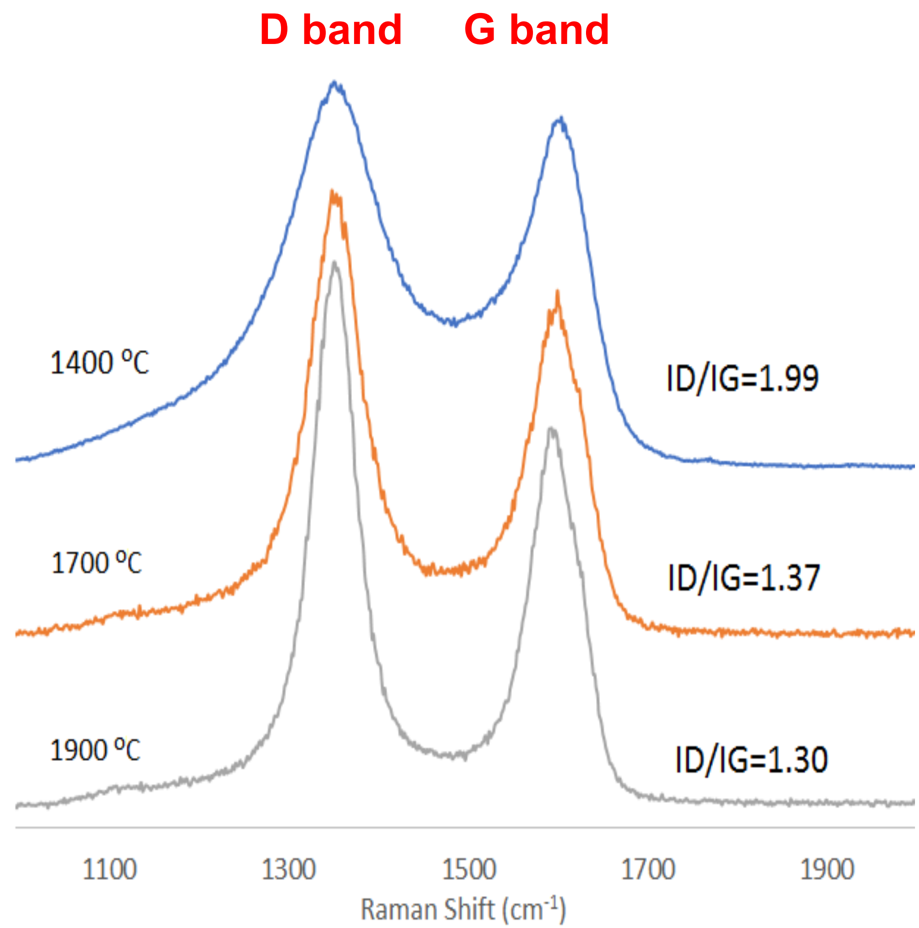
Accomplishment: Raman Spectra of Resulting Carbon Fibers

(carbonization at 1400, 1700, 1900 °C for 1h under N_2)

From PE-g-Pitch precursor with 79% free Pitch (Sample 1)



From PE-Pitch precursor with 40% free Pitch(Sample 4)



The integrated intensity ratio ($R=I_D/I_G$) for PAN-based carbon fibers is about 1

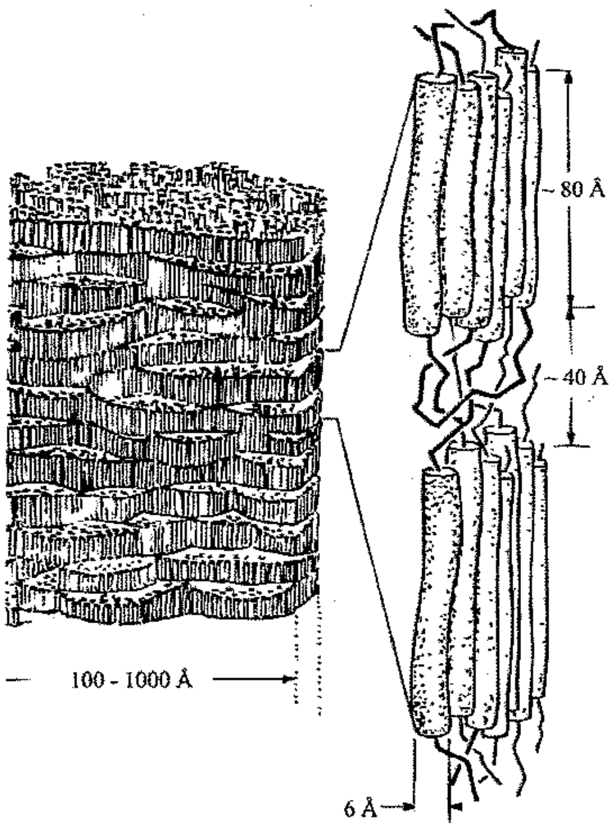
Milestones and Deliverables Summary Table

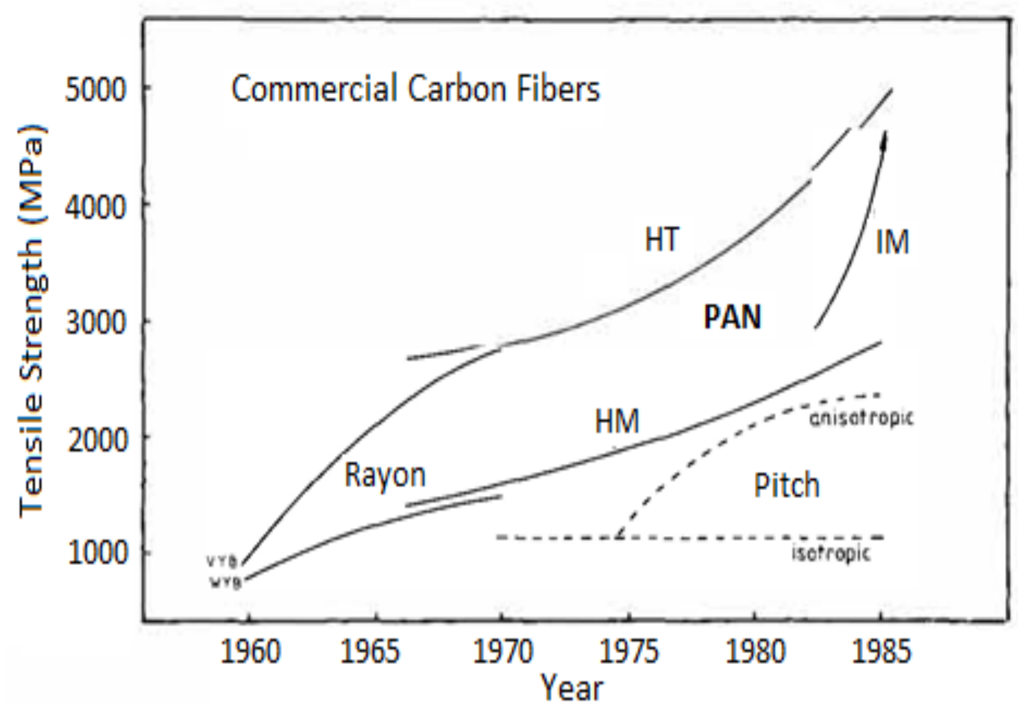
Recipient Name: T. C. Mike Chung

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 by ^{1}H and ^{13}C NMR spectra	^{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 by GPC curves and ^{1}H NMR spectra	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 by GPC curves and ^{1}H NMR spectra	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 (yield >80%) after pyrolysis at 1500 °C	Mass yield, TEM, XRD, elemental analysis.	8-12	2-4
1st Go/No-Go Decision on Precursor development for low-cost, high-strength carbon fiber		**New polyolefin precursors that can be efficiently prepared with high yields (>70%) and transformed to C with mass yield (>80%), more than 60% higher than that of current PAN with mass yield (<50%).**			Send 10 slides to LightMat /DOE summarizing all results demonstrating >80% C- yield.	The end of M12	The end of Q4
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 Videos	16-21	6-7
5.2	Carbonization of Polyolefin Fibers	Milestone	M5.2	New polyolefin based CF products	TEM, SEM, XRD, Raman, and elemental analysis .	19-24	7-8
2nd Go/No-Go Decision on Precursor development for low-cost, high-strength carbon fiber		**New low-cost and high-quality carbon fiber prepared by a combination of polyolefin precursor and melt-spinning process. The resulting polyolefin-based CFs shall exhibit similar nano-polycrystalline morphology presented in current high tensile strength PAN-based carbon fibers.**			Send 10 slides to LightMat /DOE summarizing all experimental results. Fiber samples will be provided to DOE for independent verification if requested.	The end of M24	The end of Q8
6.1	Developing a New Carbonization Process under Mechanical Tension	Milestone	M6.1	A new carbonization system with mechanical tension	TEM, SEM, Raman, XRD, and Instron results.	25-30	9-10
6.2	Carbonization of PE-Pitch (with or without free Pitch) Precursor Fibers under Tension	Milestone	M6.2	New CF converted from PE-Pitch fiber shows tensile strength >3 GP	Raman, XRD, and Instron results.	30-33	10-11
6.3	Identifying Suitable Process Condition for Carbonization of PE-Pitch Precursor Fibers under Tension	Milestone	M6.3	Improve carbonization condition to achieve tensile strength >4.5 GPa	Raman, XRD, and Instron results.	33-36	11-12
Final Project Objective		**New low-cost polyolefin-based CFs that can exhibit mechanical property like Toray T700S fiber, with 4.9 GPa tensile strength and 230 GPa tensile modulus.**				The end of M36	The end of Q12

Future: High tensile strength CFs

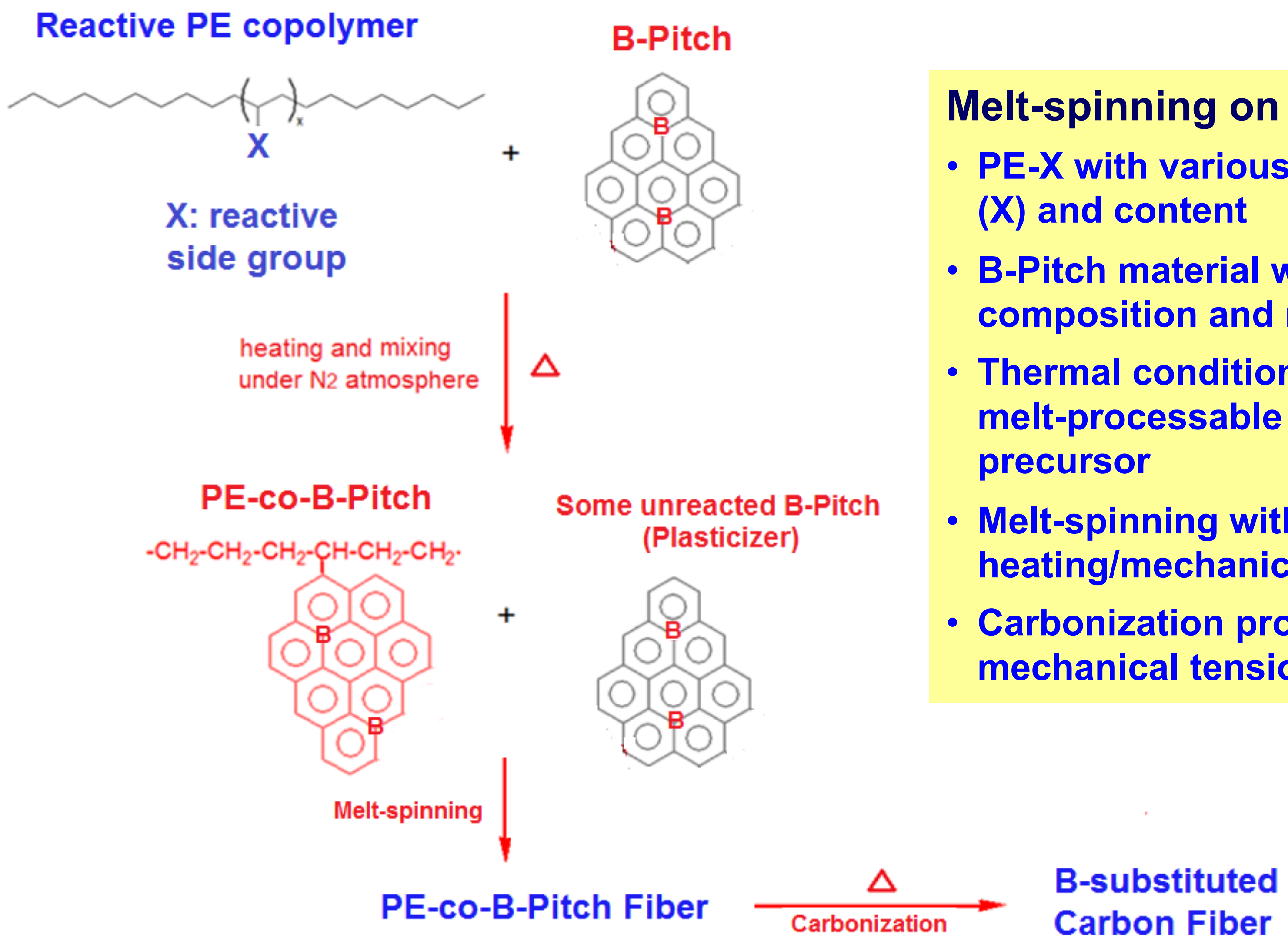




Nano-polycrystalline √
Order-disorder ratio √
Structure defects (voids)
Orientation of basal line
Fiber diameter

- *Carbonization under mechanical stretching (tension) to remove defects, orient basal line, and control fiber diameter*
- *Control heating and winding rates*

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

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

Summary

In this research project, we have developed a new class of polymer precursors based on a PE-g-Pitch graft copolymer containing PE backbone and Pitch side chains with some free Pitch molecules (serving as plasticizer and precursor).

Several potential benefits of this PE-Pitch precursor over current PAN precursor.

1. **Low material cost: inexpensive PE and Pitch**
2. **Low processing cost: melt-spinning process**
3. **Low thermal conversion cost: one-step heating under N_2**
4. **Uniform thermal conversion from fiber core to the surfaces**
5. **Higher carbon conversion yield**
6. **Resulting similar nano-polycrystalline carbon fiber morphology**

Future Research: Thermal conversion under tension (stretching) to align graphene nano-crystals (order phase) and C chains (disorder phase) along the fiber direction and reduce structural defects (voids).