

# Cost-Optimized Structural Carbon Fiber for Hydrogen Storage Tanks

Amit Naskar, Felix Paulauskas, Logan Kearney, Bob Norris,  
Michael Toomey, Shin Zhou, David McConnell  
Oak Ridge National Laboratory

Kevin Simmons, Yao Qiao  
Pacific Northwest National Laboratory

June 6, 2023

ORNL is managed by UT-Battelle, LLC for the US Department of Energy

DOE Hydrogen Program

2023 Annual Merit Review and Peer Evaluation Meeting

**Project ID # ST240**

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

# Project Goal

Manufacture low-cost, high-strength carbon fiber (CF) costing < \$15/kg, delivering target 700 ksi tensile strength and 33 Msi tensile modulus

1. Apply commodity or new polyacrylonitrile (PAN)-based precursor synthesis, spinning, conventional and advanced plasma-based processing, and fiber performance-dependent tank design technologies that will enable performance enhancement along with significant cost reduction.
2. Reduction of compressed hydrogen storage cost via novel precursor and processing technologies to manufacture low-cost, high-strength carbon fiber (CF) costing < \$15/kg, delivering target 700 ksi tensile strength and 33 Msi tensile modulus via controlled morphologies



Panoramic view of precursor fiber solution spinning capability.

# Overview

## Timeline and Budget

- Project Start Date: 4/01/2021
- Planned Completion Date: 3/31/2024
- FY21-22 DOE Funding: \$4,000,000
- FY23 Planned DOE Funding: \$2,000,000
- Total DOE Funds Received to Date\*:  
\$4,000,000

\* As of ~ 04/01/2023

## Barrier

- Manufacturing high-performance CF is a cost intensive processing. This project approach targets higher performance at lower cost.
- Enhancing fiber-matrix load translation efficiency

## Partners

- Project lead – Amit Naskar, PI ORNL
- Track Leaders
  - ❖ Thrust 1 – Translational Research
    - Felix Paulauskas, ORNL
    - Bob Norris, ORNL
    - Truman Bonds, 4XT
  - ❖ Thrust 2 – Foundational Research
    - Amit Naskar, ORNL
    - Logan Kearney, ORNL
    - Mike Toomey, ORNL
    - Shin Zhou, ORNL
  - ❖ Cross-Cutting Research
    - Kevin Simmons, PNNL
    - Yao Qiao, PNNL
    - David McConnell, ORNL

# Potential Impact

Cost-effective high pressure compressed gas storage is critical for widespread utilization of Hydrogen in Vehicles



- CF cost accounts for approximately 50% of total vehicle high pressure storage system cost
- The baseline commercial fiber in high pressure storage ranges *from \$26-30/kg CF*
- To enable hydrogen storage on board vehicles, CF cost would need to be *reduced to approximately \$13-15/kg CF*

Cost of CF is split between the cost of the precursor fiber and the cost of converting the precursor fiber to CF.

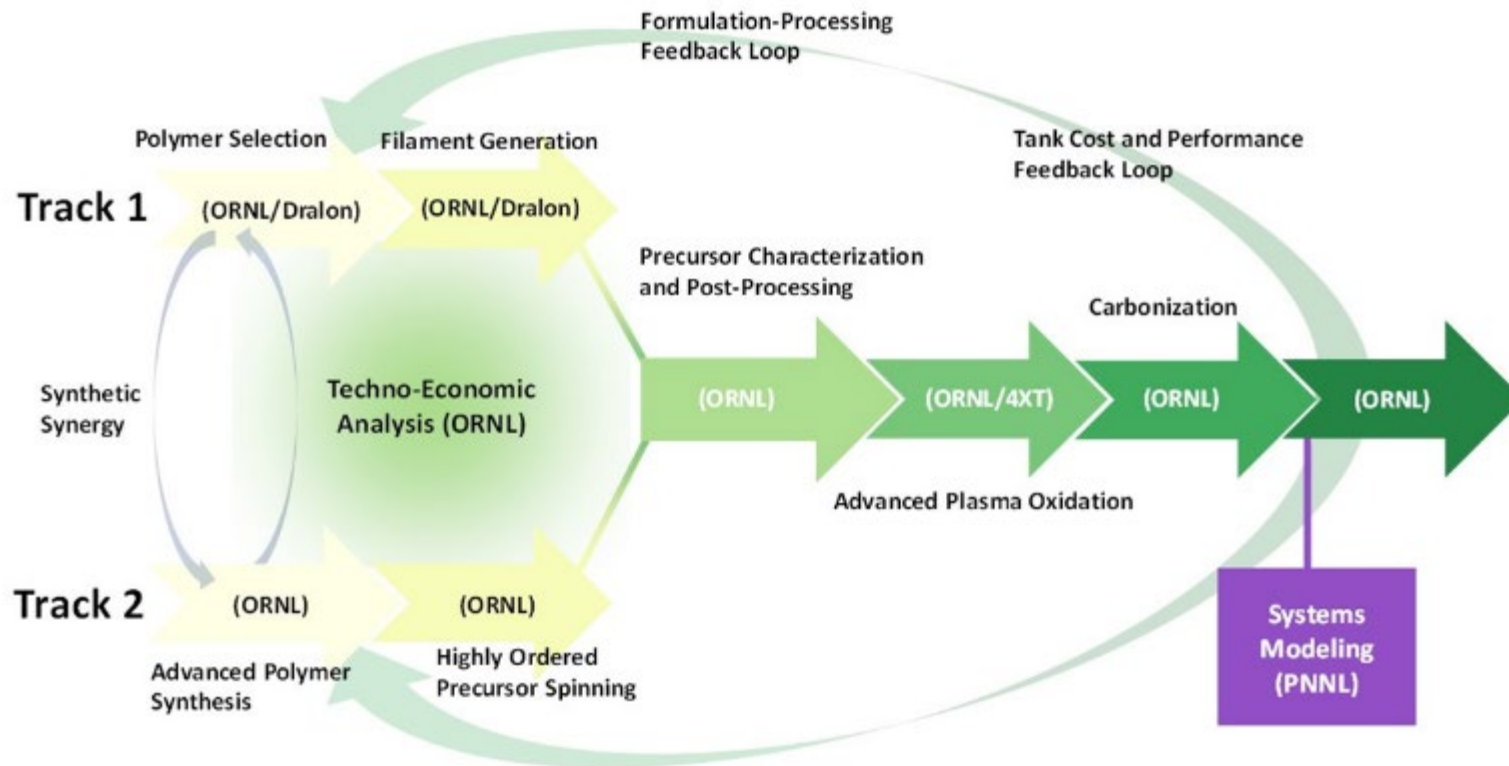
- Cost reductions will be required in both the precursor and conversion processes.
- DOE has previously supported R&D on novel advanced conversion processes with potential to enhance low-cost, high-strength CF and lower cost precursors, but very little focused research on
  - *Advancing the lower cost precursor capability towards higher performance fiber*
  - *Developing new chemical formulation approaches specifically targeting higher performance at lower cost.*

***This project addresses both approaches to achieve more cost-effective precursor and combines the best findings with advanced conversion for optimal savings***

# Approach

Our work utilizes a two-prong approach:

- **Thrust 1 (High TRL Track):** Translational research with semi-commercially produced commodity-grade polyacrylonitrile (PAN)-based carbon precursor fiber using both conventional and advanced conversion methodologies for cost and performance optimization; and
- **Thrust 2 (Low TRL Track):** Foundational research to enhance processability of newly synthesized PAN precursors with precise molecular architecture, high throughput cyclization and formation of high-strength carbonized filaments with controlled morphology via optimal conversion technologies to be developed in Thrust 1



## Key Milestone

**Go/No-go based on CF performance achieving tensile strength >700ksi**

**Carbon fiber in 100 filaments and length at least 100m exhibit targeted strength goals over 700 ksi**

**12/31/2022**

# Thrust 1- High TRL Focusing on Expanding/Exploiting Textile-Equivalent Acrylic Benefits

- Background - textile acrylic fiber production is largely similar to precursor
  - AN content for textiles is typically <93% vs >95% for precursor
  - Tow count is typically >100K for textiles and <50K for precursor
  - Largest co-monomer is almost exclusively methyl acrylate (MA) for precursor but may be vinyl acetate (VA) for textile. Smaller amounts of other modifiers such as itaconic acid or MMA may be used to enhance cross-linking control for precursor, but NA for textiles.
- Precursor development approach
  - Exploit inherently lower cost textile production approach as much as possible in balancing cost/performance tradeoffs
  - Higher AN, higher MW, and lower PDI improve fiber performance with penalties to production speed and difficulty along with lower mechanical yield
  - Higher tow sizes and fiber diameter enhance throughput, but more difficult to achieve targeted performance and maintain quality

# Thrust – 2: Low TRL Track

- **Thrust 2 (Low TRL Track):** Foundational research to **enhance processability** of newly synthesized PAN precursors with precise molecular architecture, **high throughput cyclization** and **formation of high-strength carbonized filaments** with **controlled structure/morphology via optimal conversion technologies** to be developed in Thrust 1

**Enhance processability** – *NMR exploration of polymer-solvent interactions for optimal chain mobility and processing*

**High throughput cyclization** – *DFT simulation exploring strategies for reducing cyclization energy barrier*

**Controlled structure/morphology via optimal conversion technologies** – *stabilization protocol optimization via RSA isoforce, isostrain experiments*

**Formation of high-strength carbonized filaments** – *iterative synthesis, spinning, stabilization, conversion to determine next steps in reaching 700 ksi milestone*

# Thrust 1—Accomplishments and Progress: Other Tools in Thrust 1 Toolbox Also Support Thrust 2

- Very good properties with Atmospheric Plasma Oxidized (APO) and conventionally carbonized industrial 1.5dtex precursor

Fv #	Diameter (μm)	Diameter Calculated	Density (g/cc)	Break Stress (Ksi)	Modulus (Msi)	Strain (%)
3201 Pre	12.70 (0.74)	12.62	1.1787 (.0001)	59.71 (5.64)	1.29 (0.14)	18.08 (1.78)
3591 ox	8.32 (0.23)	8.06	1.3634 (.0002)	40.11 (2.10)	1.13 (0.03)	18.93 (2.16)
3621*	4.82 (0.29)	4.82	1.7761 (.0007)	582.30 (75.35)	34.33 (0.61)	1.63 (0.19)
3622	4.66 (0.26)	4.82	1.7738 (.0005)	617.26 (66.79)	35.55 (0.63)	1.67 (0.16)
3623	4.54 (0.21)	4.77	1.7781 (.0084)	580.06 (68.15)	35.78 (0.97)	1.57 (0.17)
3624	4.63 (0.27)	4.79	1.7690 (.0079)	605.73 (49.47)	35.34 (0.95)	1.64 (0.11)
3625	4.76 (0.24)	4.82	1.7746 (.0005)	592.07 (67.97)	34.04 (0.71)	1.67 (0.16)
3626	4.82 (0.24)	4.89	1.7717 (.0003)	589.02 (57.51)	32.96 (0.61)	1.71 (0.14)

*Industry standard impregnated strand data is typically 8-10% higher than average single filament data meaning we are rapidly approaching project performance target of 700ksi.*

- Fully conventional conversion and larger diameter properties are good, but not yet compatible with targets

# Contracted Developmental Precursor Status

- Initial work is promising with the newest materials

Fully Conventional Conversion

Fv #	Diameter (μm)	Diameter Calculated	Density (g/cc)	Break Stress (Ksi)	Modulus (Msi)	Strain (%)
Precursor	12.76 (1.12)	13.09	1.1679	95.17 (8.31)	1.97 (0.14)	12.10 (0.75)
Oxidized	11.32 (1.22)	11.28	1.3339	58.46 (5.67)	1.66 (0.07)	12.80 (2.19)
4369	6.79 (0.41)	6.00	1.8153	464.13 (70.15)	35.02 (0.43)	1.29 (0.19)
4370	6.55 (0.46)	6.58	1.8342	476.73 (97.50)	34.90 (0.81)	1.33 (0.24)
4377	6.51 (0.54)	6.65	1.8371	438.65 (93.78)	35.12 (0.50)	1.22 (0.24)
4378	6.68 (0.45)	6.73	1.8334	501.29 (66.94)	34.48 (1.03)	1.42 (0.19)
4379	6.93 (0.40)	6.74	1.8340	410.52 (43.78)	33.86 (0.57)	1.20 (0.12)

APO Oxidation Conventional Carbonization

Fv #	Diameter (μm)	Diameter Calculated	Density (g/cc)	Break Stress (Ksi)	Modulus (Msi)	Strain (%)
Oxidized	9.47 (0.79)	9.56	1.3609	70.62 (4.05)	1.77 (0.05)	11.01 (1.01)
4335	6.41 (0.41)	6.03	1.8190	420.12 (92.68)	34.33 (1.33)	1.20 (0.24)
4336	6.04 (0.46)	6.10	1.8213	471.16 (94.97)	34.15 (1.73)	1.34 (0.24)
4337	6.13 (0.55)	6.07	1.8206	469.59 (80.97)	34.67 (2.10)	1.32 (0.18)
4338	5.85 (0.62)	5.98	1.8244	509.34 (65.03)	35.47 (1.07)	1.40 (0.18)
4339	5.92 (0.55)		1.82**	403.87 (49.89)	35.95 (0.84)	1.11 (0.13)

- Both conversion approaches provide similar results

# Alternative Commercial Precursor

Fv #	Diameter (μm)	Diameter Calculated	Density (g/cc)	Break Stress (Ksi)	Modulus (Msi)	Strain (%)
3711 Pre	11.00 (0.26)	10.83	1.1809 (.0002)	102.59 (14.88)	2.16 (0.04)	11.42 (1.53)
3731 Ox	10.65 (0.38)	10.19	1.4024 (.0002)	42.02 (3.24)	1.38 (0.03)	16.53 (2.83)
3732	6.16 (0.22)	6.46	1.7657 (.0004)	584.05 (126.78)	38.01 (0.38)	1.49 (0.31)
3733	6.21 (0.22)	6.29	1.7735 (.0006)	634.62 (114.09)	38.43 (0.55)	1.59 (0.27)
3734	6.11 (0.28)	6.34	1.7737 (.0006)	648.63 (95.38)	38.06 (1.03)	1.64 (0.24)
3735	6.59 (0.27)	6.59	1.7394 (.0014)	589.17 (92.67)	36.25 (0.51)	1.57 (0.23)
3736	6.65 (0.31)	6.64	1.7667 (.0007)	629.26 (110.18)	36.59 (0.65)	1.66 (0.27)
3737	6.46 (0.33)	6.65	1.7683 (.0004)	630.67 (155.56)	37.64 (0.55)	1.63 (0.38)
3738	6.74 (0.24)	6.69	1.7677 (.0004)	584.54 (72.09)	36.99 (0.55)	1.54 (0.17)
3740	6.69 (0.25)	6.80	1.7630 (.0024)	585.91 (97.16)	36.28 (0.50)	1.56 (0.24)
3741	6.72 (0.28)	6.97	1.7616 (.0005)	593.46 (131.54)	35.54 (0.55)	1.61 (0.34)

Fv #	Diameter (μm)	Diameter Calculated	Density (g/cc)	Break Stress (Ksi)	Modulus (Msi)	Strain (%)
3711	11.00 (0.26)	10.83	1.181	102.59 (14.88)	2.16 (0.04)	11.42 (1.53)
3705	10.11 (0.83)	10.39	1.3416	57.13 (7.04)	1.69 (0.20)	13.18 (1.82)
3699	6.00 (0.24)	6.18	1.8142 (.0010)	641.09 (123.60)	36.33 (1.81)	1.68 (0.30)
3700	6.15 (0.36)	6.10	1.8128 (.0004)	570.26 (139.17)	35.56 (2.07)	1.54 (0.32)
3701	5.96 (0.22)	6.09	1.8126 (.0004)	669.85 (107.09)	37.44 (1.67)	1.70 (0.24)
3702	6.07 (0.29)	6.13	1.8076 (.00030)	623.84 (162.17)	37.79 (2.91)	1.57 (0.34)
3703	5.88 (0.30)	6.39	1.8028 (.0004)	655.46 (125.77)	38.78 (3.49)	1.62 (0.26)
3704	5.83 (0.28)	6.37	1.8031 (.0004)	735.29 (126.19)	41.37 (3.28)	1.70 (0.21)
3707	6.47 (0.27)	6.59	1.8018 (.0005)	608.32 (104.09)	32.36 (1.58)	1.81 (0.33)
3708	6.36 (0.24)	6.54	1.8007 (.0021)	667.02 (95.11)	35.22 (1.36)	1.81 (0.23)
3709	6.22 (0.23)	6.48	1.8014 (.0004)	632.58 (116.86)	34.61 (1.34)	1.75 (0.30)
3710	6.52 (0.26)	6.53	1.8031 (.0003)	606.12 (92.86)	32.25 (1.69)	1.80 (0.24)

- Both conversion approaches provide Excellent results!
- Reminder that *strand data is typically 8-10% higher than average single filament data*

## Fully Conventional Conversion

- Although this could be a very good approach, we have little knowledge on precursor long-term availability and cost

## APO Oxidation Conventional Carbonization

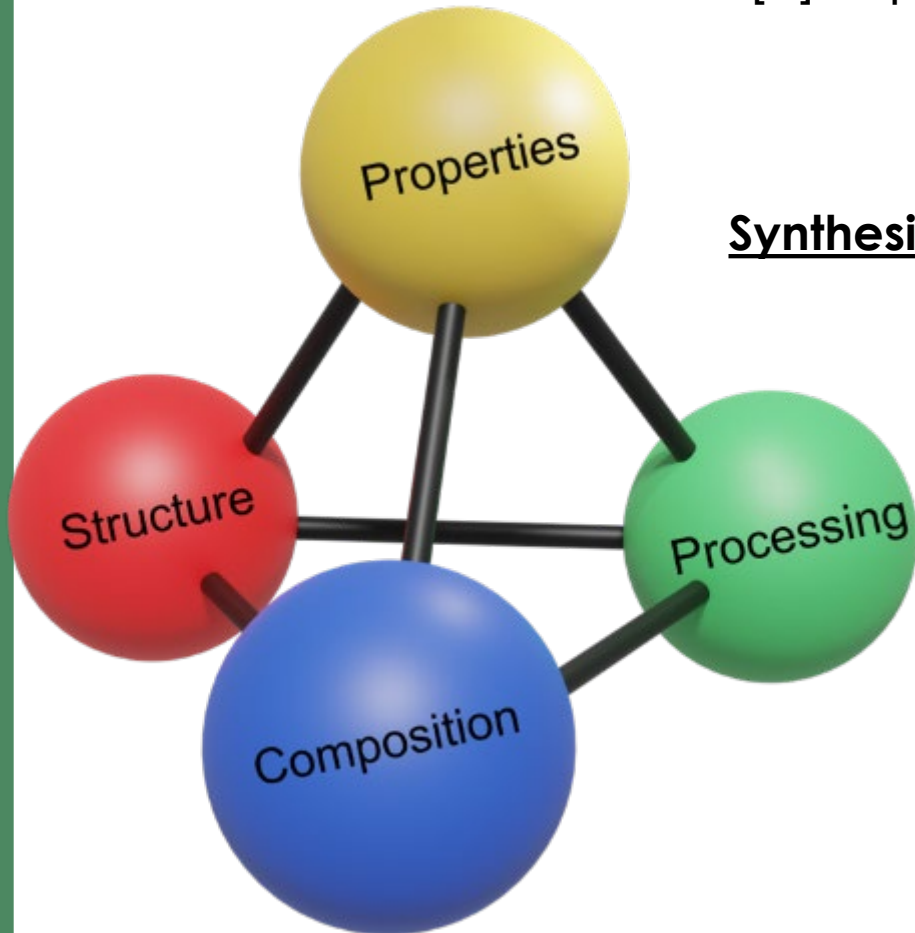
# Thrust 2 – Design motifs in PAN for High-Performance CFs

Polymer design for carbon fibers requires precise control of a multi-variable, inter-dependent phase space

Polymer - MW, PDI, [AN:M<sub>x</sub>:M<sub>y</sub>] | Precursor Fiber – ε, E, X<sub>c</sub>, f | OPF – Ø, ρ, f → CF Properties

Cost optimized fiber design needs to balance antagonistic materials and process variables

MW and [C] ∝ η ; [C] and Ø ∝ \$ ; [AN] ∝ CED vs σ<sub>Tensile</sub>

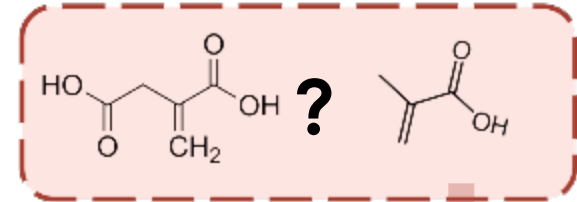
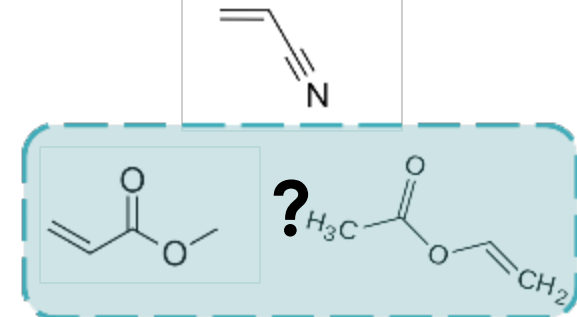


Synthesis @ ORNL

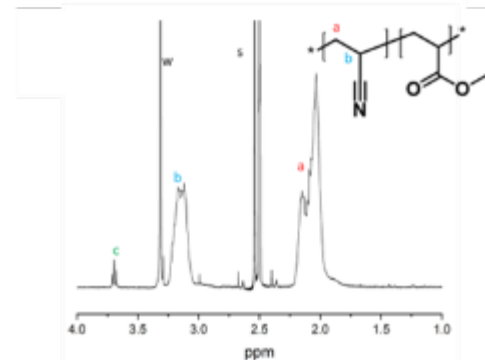
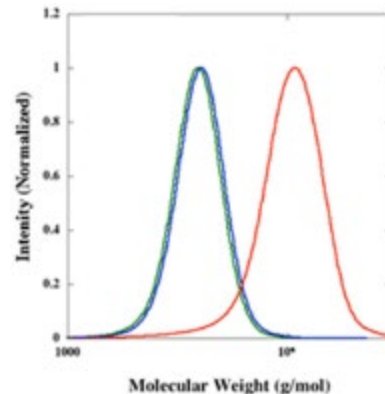


0.1 – 5L Scale Solution

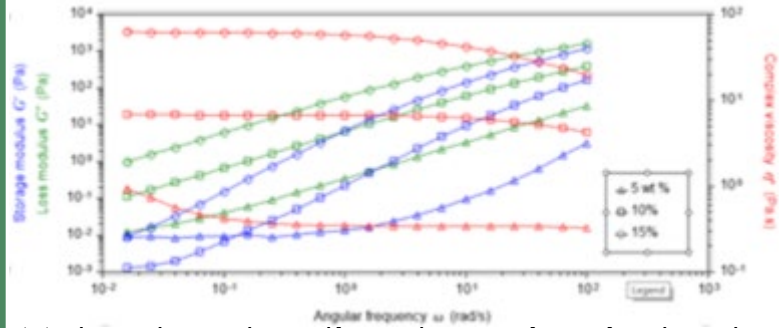
Composition optimization



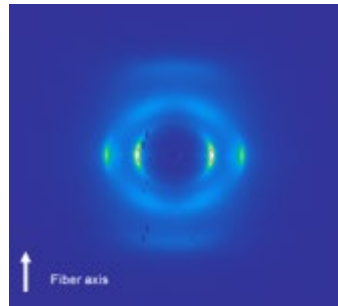
10 -20 L Scale Dispersion



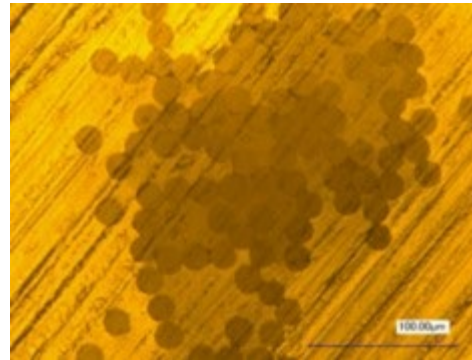
# Thrust 2—Accomplishments and Progress: Fiber fabrication and post processing



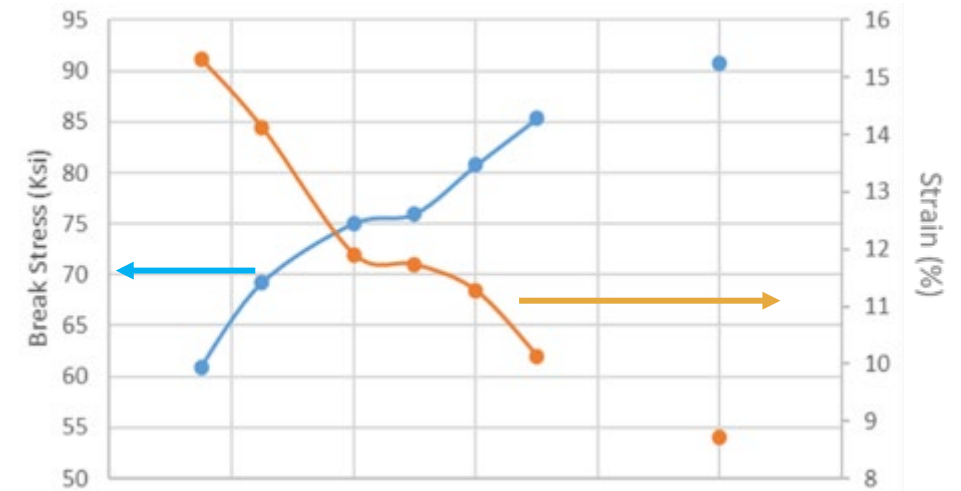
Molecular relaxation dynamics via rheology



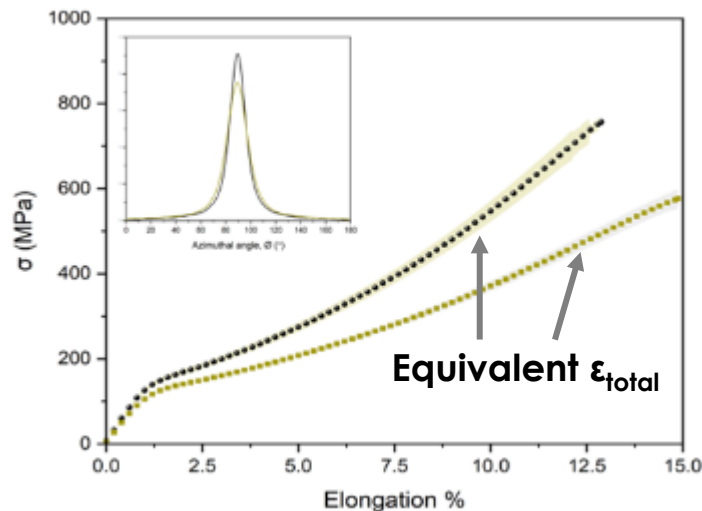
**2D WAXS**  
Spinning process – structure evolution



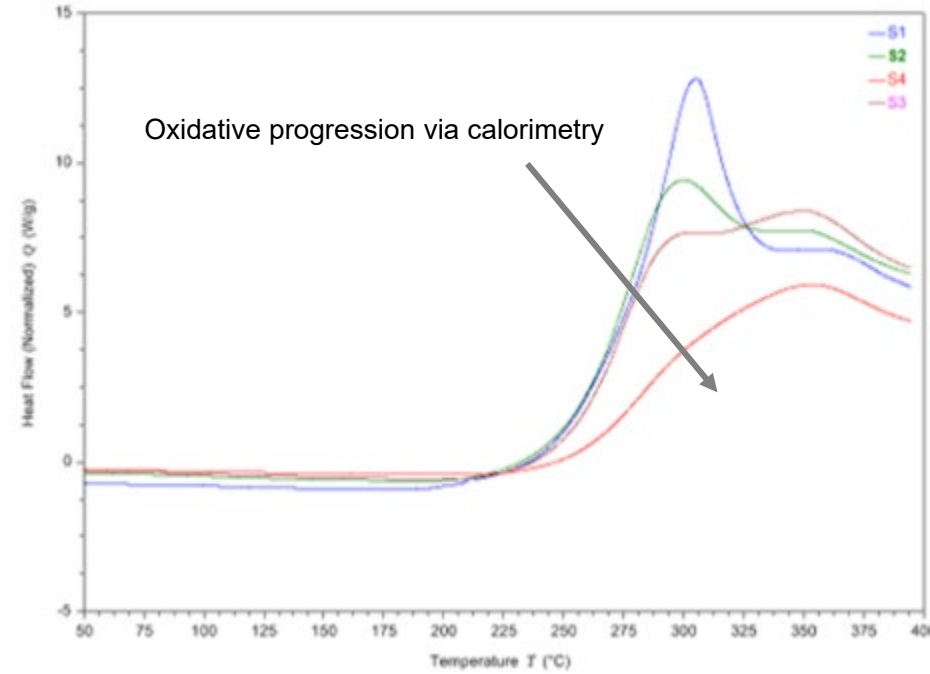
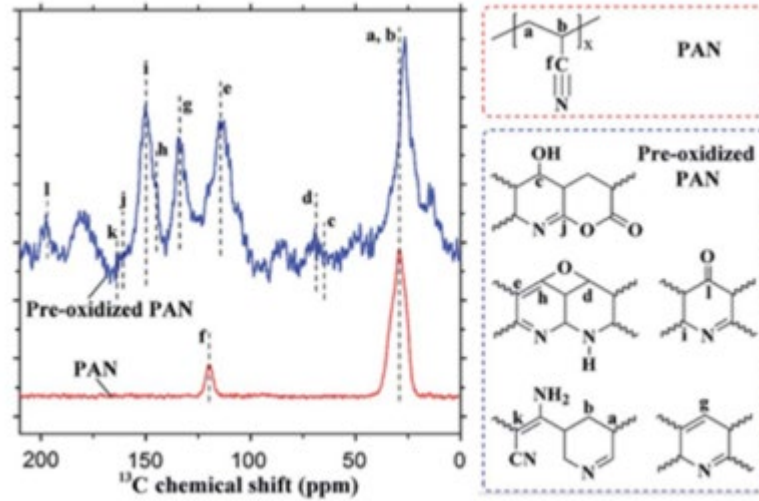
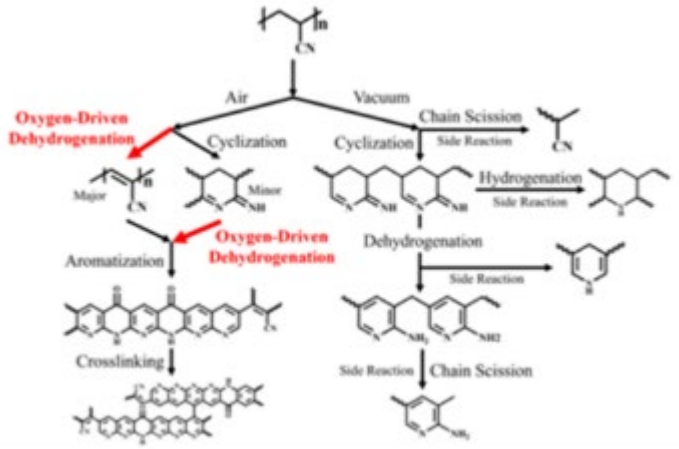
Precursor fiber conditioning can enable a wider range of fiber quality to achieve high performance CF



Macromolecular ordering via secondary deformations

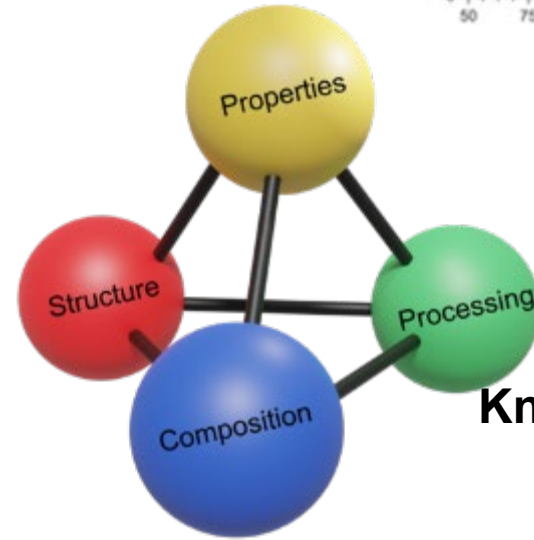
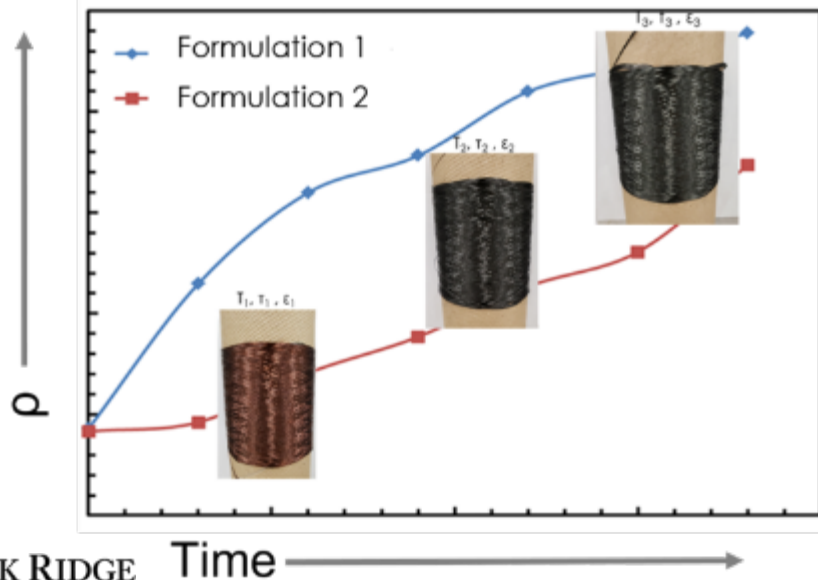


# Thrust 2—Accomplishments and Progress: Conversion has composition and structure dependent dynamics



Macromolecules 50.1 (2017): 244-253.

Fiber chemistry dictates time dependent structural evolution



Knowledge built from Thrust 2 will reinforce Thrust 1 formulation and process enhancements

# Thrust 2—Accomplishments and Progress

- Recently demonstrated 150 kDa PAN precursor molecular weight with high yield (>60% conversion in polymerization of AN) for new precursor developed specifically for this project
- Acquired baseline textile-based precursor having >10% elongation. Completed characterization of this precursor and initial processing conditions identified; oxidized fiber delivers 1.36 g/cc density
- Developing path for enhanced interfacial interaction between fiber and epoxy matrix.

Sample	%EL at Failure	Break Stress (ksi)	Modulus (Mpsi)
1	1.386071	547.0355	43.22249
2	1.43208	524.4526	36.18613
3	1.47612	513.3752	34.53305
4	1.48415	504.1096	33.69372
5	1.40808	496.985	35.53799
6	1.41415	478.4041	36.46622
7	1.46804	489.3448	33.53422
8	1.41404	495.0222	34.57769
9	1.42608	475.9566	35.20317
10	1.37802	483.3545	35.81152
11	1.45812	484.1576	32.69368
12	1.40402	487.3651	34.1547
13	1.44002	465.8409	34.38446
14	1.38003	486.4044	34.64733
15	1.404218	481.1254	33.65942
16	1.50007	453.2992	32.45328
17	1.402184	481.5163	33.26076
18	1.40802	463.69	33.89963
19	1.380093	466.6139	34.4446
20	1.27205	474.6488	37.02224

Samples underwent unique oxidation (stretch, temperature), Low temperature conversion (stretch, residence time), and high temperature conversion (stretch, residence time) before being assessed for their final properties, to optimize process. 56 samples processed; top 20 performers shown above.

# CF performance:

Samples underwent unique oxidation (stretch, temperature), Low temperature conversion (stretch, residence time), and high temperature conversion (stretch, residence time) before being assessed for their final properties, to optimize process. >100 samples processed in total; top 10 performers for each respective category (modulus, break strength, elongation, etc.) in green.

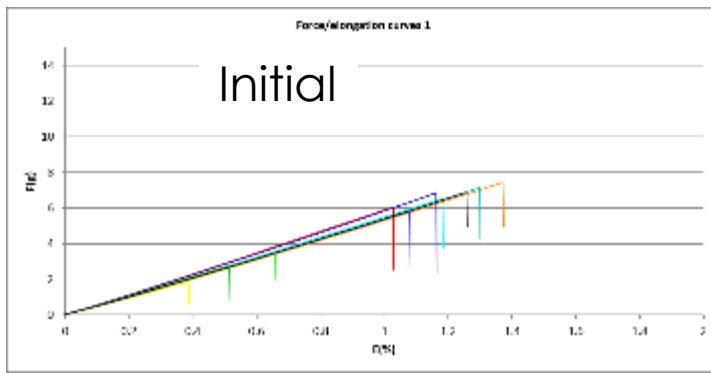
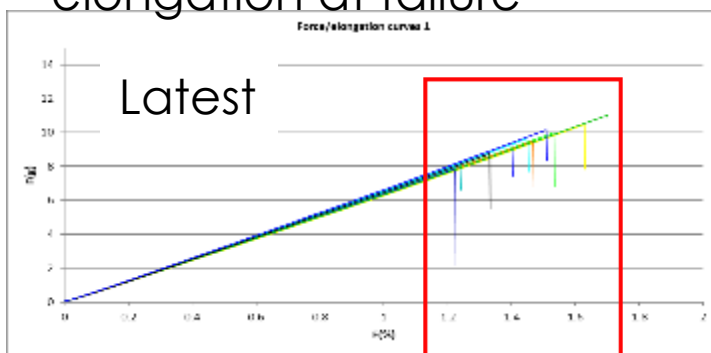
Through dope, spinning, oxidation, and conversion optimization, recent samples have shown continual improvement, though break stress still has yet to surpass 700 ksi.

Elongation initial: 0.99-1.10%  
Most recent elongations: 1.32-1.45%

Break stress initial: 310-350 ksi  
Most recent break stresses: 490-550 ksi

Mod initial: 28.9-33.0 Mpsi  
Most recent mod: 31.5 – 32.15 Mpsi  
Highest modulus: 35.6 Mpsi

→ Increased loading for terpolymer improved elongation at failure



Condition	Sample set	Rank	Rank	Rank	Rank	Rank	Rank	Rank	Rank
Sample		%EI_ave	%EI_max	Break_ave	Break_ma	Mod_ave	Mod_max	MAG_ave	MAG_max
HT5	JC-S4-C2a-15xR1	1	2	1	2	3	67	24	1
HT4	JC-S4-C2a-15xR1	2	1	2	1	5	61	1	3
5-90/-6-90	S2-C2R2	3	6	3	9	34	44	2	10
5-90/-3-90	S2-C2R2	5	31	4	21	20	21	4	25
10-90/-2-90	S2-C2R2	10	12	5	16	4	5	3	8
10-90/-4-90	S2-C2R2	8	25	6	13	7	11	5	12
8-90/-6-90	S2-C2R2	4	4	7	6	35	40	6	6
8-90/-4-90	S2-C2R2	7	47	8	37	27	36	8	43
10-90/-3-90	S2-C2R2	17	52	9	18	1	2	7	19
10-90/-5-90	S2-C2R2	16	14	10	7	6	14	9	7
8-90/-5-90	S2-C2R2	13	5	11	5	15	26	10	5
8-90/-3-90	S2-C2R2	11	22	12	23	33	39	12	26
5-180_-5-90	second	6	27	13	32	45	47	11	34
14-180_-2-90	second	9	15	14	26	44	37	13	23
5-90/-4-90	S2-C2R2	21	17	15	10	17	32	14	13
8-90/-2-90	S2-C2R2	19	32	16	25	24	33	16	27
5-90_0-90	second	20	58	17	42	23	20	17	48
12-90/-2-90	S2-C1R3	37	46	18	19	2	4	15	21
14-90_-3-120	second	23	55	19	36	28	27	18	44
5-90/-4-90	S2-C2R3	28	34	20	28	26	38	20	31
14-180_-2-180	second	33	45	21	47	10	6	19	36
14-120/-3-90	first	22	37	22	38	30	17	21	35
5-90/-5-90	S2-C2R3	34	21	23	3	14	1	23	2
5-90/-5-90	S2-C2R2	32	33	24	20	16	24	22	24
17-90/-7-90	first	14	20	25	33	58	51	25	33
5-90_+2-90	second	24	38	26	41	42	43	26	41
14-120/-7-90	first	15	9	27	44	62	64	29	38
14-90_-3-180	second	30	54	28	43	36	3	28	37
14-120/-5-90	first	38	35	29	27	18	19	27	28
8-90/-6-90	THIRD	26	7	30	12	50	56	32	14
11-60/-5-90	first	25	41	31	53	43	58	30	54
5-90_-2-90	second	36	50	32	46	29	25	31	45
5-90/-3-90	S2-C2R3	39	16	33	15	31	42	33	17
14-180_-5-90	second	27	49	34	51	57	55	36	53
14-90/-7-90	first	12	3	35	29	68	62	37	20
10-90/-6-90	S2-C2R2	47	13	36	8	19	23	34	9
8-90/-7-90	first	18	29	37	35	63	66	35	42
5-180_-2-180	second	41	61	38	54	32	28	38	58
17-90/-3-90	first	46	63	39	48	25	15	39	50
8-120/-3-90	first	40	57	40	60	55	59	44	61
12-90/-6-90	S2-C1R3	42	39	41	45	54	63	45	49
5-90/-7-90	first	31	51	42	62	60	45	41	60
5-90/-3-90	first	44	65	43	65	39	34	40	67
8-90/-5-90	first	35	30	44	50	56	57	43	46
11-120/-3-90	first	29	56	45	59	67	68	48	64
5-90/-3-90_2	S2-C1R3	52	18	46	14	41	49	46	18
12-90/-4-90	S2-C1R3	55	10	47	4	9	10	42	4
17-90/-5B-90	first	45	28	48	40	53	13	49	29
5-90/-3-90	S2-C1R3	43	26	49	30	65	65	52	39
8-120/-7-90	first	51	36	50	34	46	53	51	40
8-90/-3-90	S2-C1R3	57	40	51	39	11	7	47	32
14-90/-5-90	first	48	19	52	31	61	50	53	30
11-60/-7-90	first	53	44	53	56	62	60	54	57
17-90/-5A-90	first	49	43	54	61	64	46	57	59
14-90_0-180	second	59	60	55	58	8	12	50	52
17-90/-5C-90	first	54	48	56	52	51	41	56	51
8-90/-4-90	S2-C1R3	58	11	57	17	22	16	55	11
11-90/-7-90	first	56	64	58	64	59	52	59	65
5-90/-2-90	S2-C2R3	62	23	59	22	13	29	58	22
5-180_-2-90	second	61	62	60	63	38	48	60	63
11-90/-5-90	first	60	42	61	49	49	35	63	47
5-90/-5-90	first	50	24	62	11	66	22	61	15
8-120/-7B-90	first	63	53	63	57	48	31	64	55
14-90_0-180-3	second	65	66	64	67	12	8	62	62
5-90/-4-90	S2-C1R3	64	67	65	66	40	54	65	68
5-90_-2-180	second	66	8	66	24	47	30	66	16
11-90/-3-90	first	67	68	67	68	37	9	68	66
5-90/-6-90	S2-C1R3	68	59	68	55	21	18	67	56

# CF performance:

Samples underwent unique oxidation (stretch, temperature), Low temperature conversion (stretch, residence time), and high temperature conversion (stretch, residence time) before being assessed for their final properties, to optimize process. >100 samples processed in total; top 10 performers for each respective category (modulus, break strength, elongation, etc.)

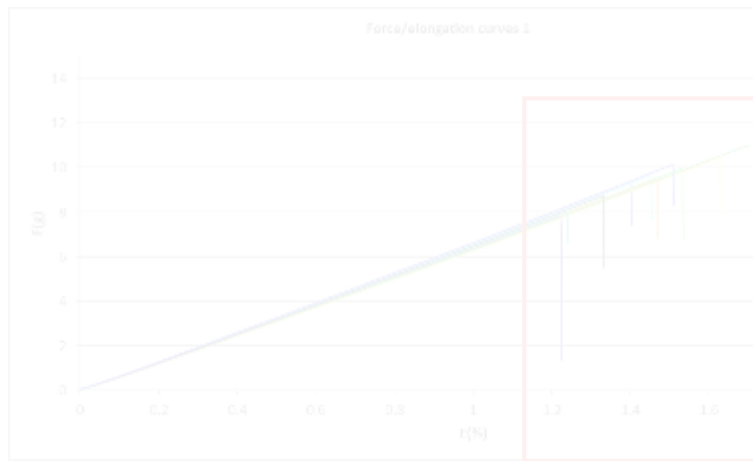
Through dope, sp...  
samples have sh...  
yet to surpass 700

Elongation initial:  
Most recent elong

Break stress initial:  
Most recent break

Mod initial: 28.9-33.0 Mpsi  
Most recent mod: 31.5 – 32.15 Mpsi  
Highest modulus: 35 – Mpsi

- High moduli are indicative of favorable carbon structure.
- Low elongation at failure attributed to internal flaws.
- Limited coagulation bath length (in-house) is thought to be responsible for internal porosity driving early failure.
- Air gap spinning using high loading will reduce porosity and is expected to result in internal structure necessary to reach 700 ksi



Sample	Condition	Rank	Rank	Rank	Rank	Rank	Rank	Rank	Rank	Rank
HT5	JC-S4-C2a-15xR1	1	2	1	2	3	67	24	1	1
HT4	JC-S4-C2a-15xR1	2	1	2	1	5	61	1	3	3
5-90/6-90	S2-C2R2	3	6	3	9	34	44	2	10	10
5-90/3-90	S2-C2R2	5	31	4	21	20	21	4	25	25
10-90/2-90	S2-C2R2	10	12	5	16	4	5	3	8	8
10-90/4-90	S2-C2R2	8	25	6	13	7	11	5	12	12
8-90/6-90	S2-C2R2	4	4	7	6	35	40	6	6	6
8-90/4-90	S2-C2R2	7	47	8	37	27	36	8	43	43
10-90/3-90	S2-C2R2	17	52	9	18	1	2	7	19	19
10-90/5-90	S2-C2R2	16	14	10	7	6	14	9	9	9
8-90/5-90	S2-C2R2	13	5	11	5	15	26	10	10	10
8-90/3-90	S2-C2R2	11	22	12	23	33	39	12	12	12
5-180_5-90	second	6	27	13	32	45	47	11	14	14
14-180_2-90	second	9	15	14	26	44	37	13	13	13
5-90/4-90	S2-C2R2	21	17	15	10	17	32	14	14	14
8-90/2-90	S2-C2R2	19	32	16	25	24	33	16	17	17
5-90_0-90	second	20	58	17	42	23	20	17	48	48
		37	46	18	19	2	4	15	21	21
		23	55	19	36	28	27	14	44	44
		28	34	20	28	26	38	13	31	31
		33	45	21	47	10	6	19	36	36
		22	37	22	38	30	17	21	35	35
		34	21	23	3	14	1	23	2	2
		32	33	24	20	16	24	22	24	24
		14	20	25	33	58	51	25	33	33
		24	38	26	41	42	43	26	41	41
		15	9	27	44	62	64	29	38	38
		30	54	28	43	36	9	28	37	37
		38	35	29	27	18	19	27	28	28
		26	7	30	12	50	56	32	14	14
		25	41	31	53	43	58	30	54	54
		36	50	32	46	29	25	31	47	47
		39	16	33	15	31	42	33	33	33
		27	49	34	51	57	55	36	53	53
		12	3	35	29	68	62	37	20	20
		47	13	36	8	19	23	34	9	9
		18	29	37	35	63	66	35	42	42
		41	61	38	54	32	28	38	58	58
		46	63	39	48	25	15	39	50	50
		40	57	40	60	55	59	44	61	61
		42	39	41	45	54	63	45	49	49
		31	51	42	62	60	45	41	60	60
		44	65	43	65	39	34	40	67	67
		35	30	44	50	56	57	43	46	46
		29	56	45	59	67	68	48	64	64
		52	18	46	14	41	49	46	46	46
		12	90	47	4	9	10	42	4	4
		45	28	48	40	53	13	49	29	29
		43	26	49	30	65	65	52	39	39
		51	36	50	34	46	53	51	40	40
		57	40	51	39	11	7	47	32	32
		48	19	52	31	61	50	53	30	30
		53	44	53	56	52	60	54	57	57
		49	43	54	61	64	46	57	59	59
		59	60	55	58		12	50	52	52
		54	48	56	52	51	41	56	51	51
		58	11	57	17	22	16	55	11	11
		56	64	58	64	59	52	59	65	65
		62	23	59	22	13	29	58	22	22
		61	62	60	63	38	48	60	63	63
		60	42	61	49	49	35	63	47	47
		50	24	62	11	66	22	61	15	15
		63	53	63	57	48	31	64	55	55
		65	66	64	67	12	8	62	62	62
		64	67	65	66	40	54	65	68	68
		66	8	66	24	47	30	66	16	16
		67	68	67	68	37	9	68	67	67
		68	59	68	55	21	18	67	66	66

# Cross-Cutting Activities – Both Tracks

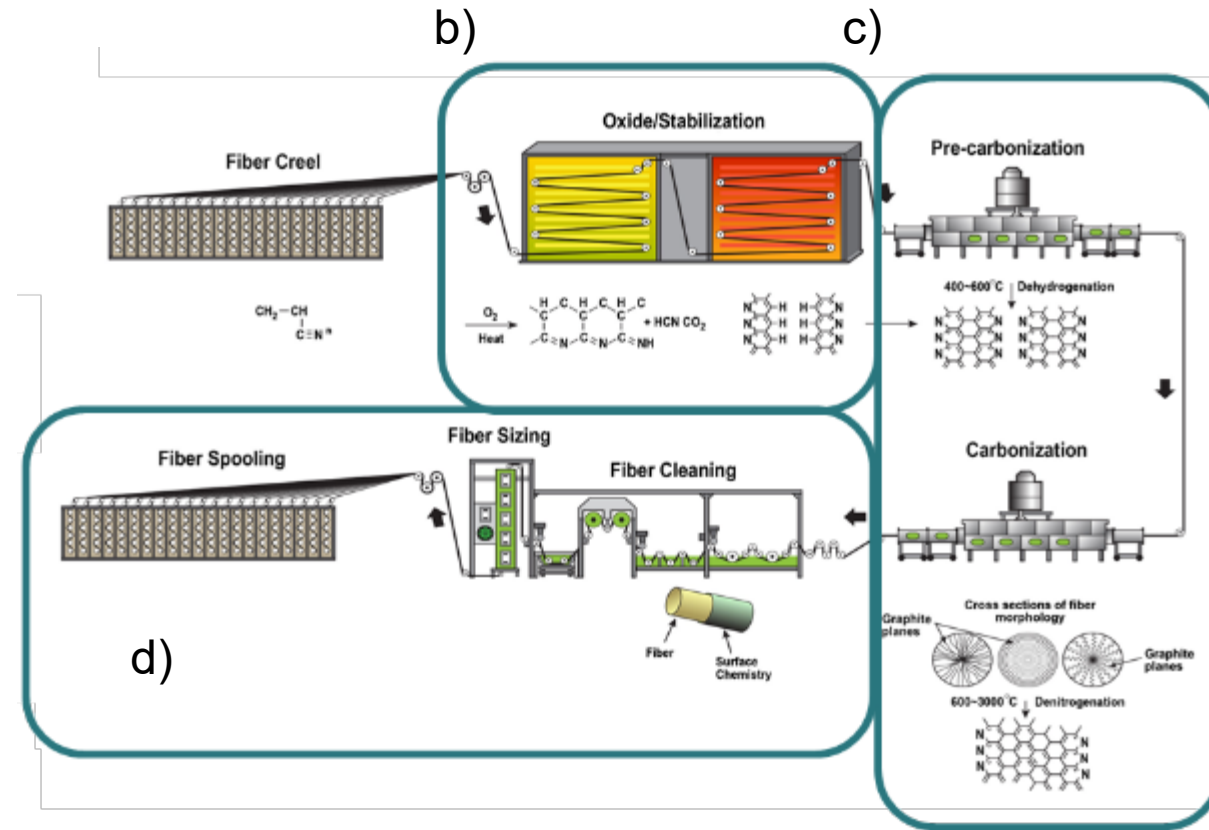
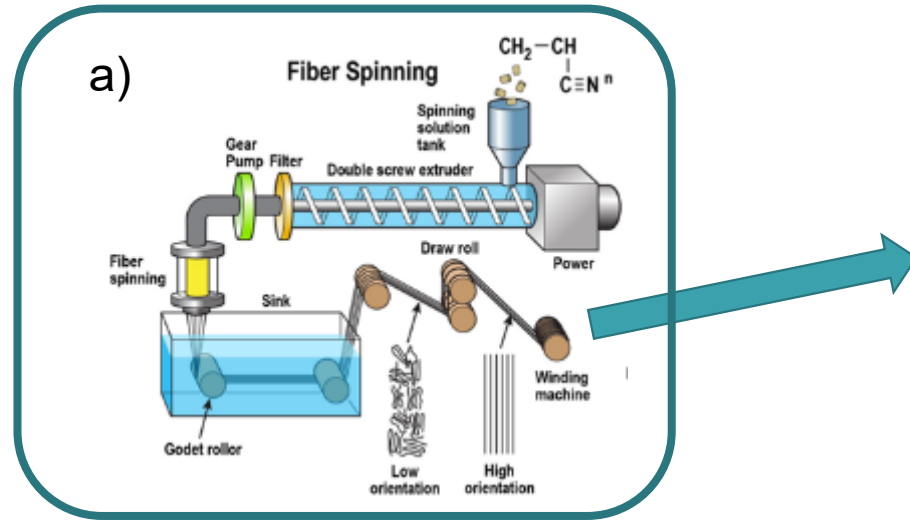


The Precursor Evaluation System for oxidizing and carbonizing very small research and development tows from 100 filaments up to 24,000 filaments in order to evaluate processability and project performance capabilities for advanced carbon fiber formulations is shown in one of ORNL's research laboratories.



Overview of 1-ton-per-year pilot line (at 4X Technologies) for fully integrated conversion of 1-4 carbon fiber tows to demonstrate conversion recipes and resulting fiber improvements.

# Accomplishments: Cost Model Structure Development



Review of prior cost studies four process elements for fiber cost analysis

- a) Precursor AN, polymerization & spinning
- b) Oxidation/stabilization
- c) Low temperature/High-temperature carbonization
- d) Post-Treatment/ Packaging

# Accomplishments: Cost Model Structure Development

Carbon Fiber Cost Model:  
Process Element-wise Cost Scenario Analysis

CF Process Element	CF Process Element Fractional Cost Ratio (%)			
	ORNL 2011 (Warren)	ORNL 2022 (Paulaskas)	Other	Average
Precursor AN, polymerization & spinning	51%	46%	48%	48%
Stabilization/ Oxidation	16%	18%	15%	16%
Carbonization (LT/HT)	23%	24%	25%	24%
Post-Treatment/ Packaging	10%	12%	12%	11%
<b>Total</b>	<b>100%</b>	<b>100%</b>	<b>100%</b>	<b>100%</b>

- Averages of prior work for each process element were averaged
- Cost reduction scenarios were evaluated to demonstrate where the most significant impact can be made
- Precursor and oxidation/stabilization are most impactful to cost and influence LT/HT cost reduction with higher furnace throughput

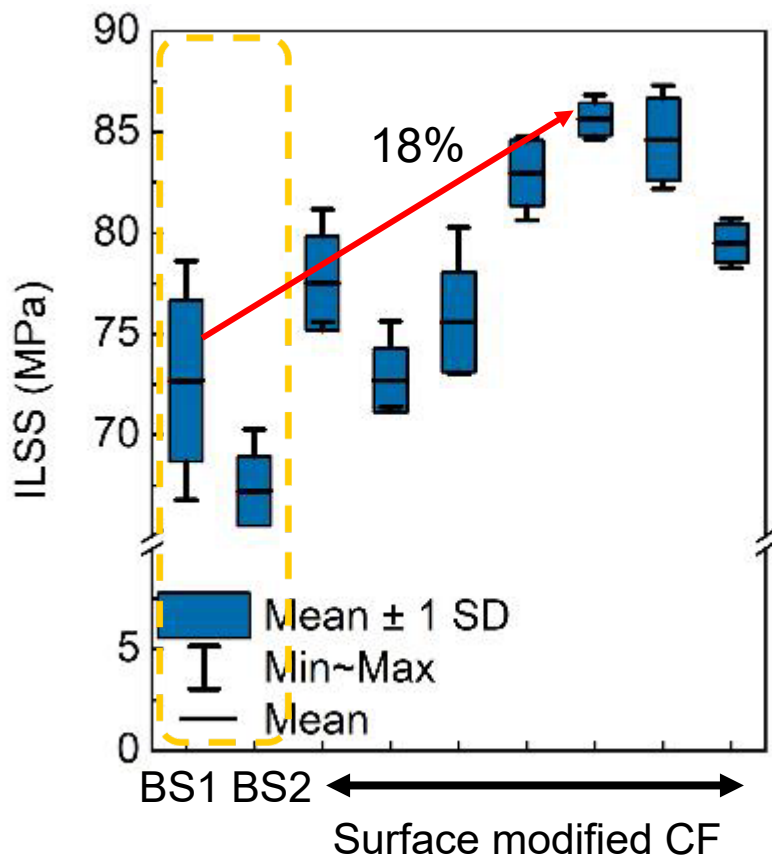
Cost Reduction Scenarios (\$/kg)

CF Process Element	Cost Ratio	Cost Reduction Scenarios (\$/kg)			
		#1 Baseline Cost	#2 -30% PC	#3 -30% PC/ -80% ORT	#4 -50% PC/ -80% ORT/ -10% LT-HT
Precursor AN, polymerization & spinning	48%	\$13.50	\$9.45	\$9.45	\$6.75
Stabilization/ Oxidation	16%	\$4.56	\$4.56	\$0.91	\$0.91
Carbonization (LT/HT)	24%	\$6.70	\$6.70	\$6.70	\$6.03
Post-Treatment/ Packaging	11%	\$3.17	\$3.17	\$3.17	\$3.17
<b>Total Carbon Fiber Cost</b>	<b>100%</b>	<b>\$27.93</b>	<b>\$23.88</b>	<b>\$20.23</b>	<b>\$16.86</b>
<b>Reduction from Baseline Cost (%)</b>		<b>0%</b>	<b>-15%</b>	<b>-28%</b>	<b>-40%</b>

Scenario #	Scenario Description
#1:	Baseline cost - Precursor cost for industrial applications (Warren)
#2:	30% reduction in precursor cost from Baseline Cost
#3:	#2 + 80% reduction in Oxidation Residence time (higher throughput)
#4	#2 + 80% reduction in Oxidation Residence time + 10% reduction in carbonization furnace time (higher throughput)

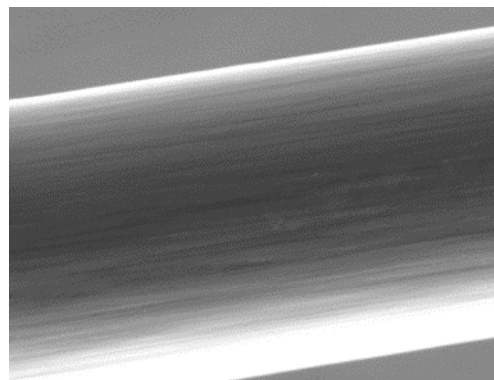
# Surface Modification of Carbon Fiber

- ❖ The carbon fiber surface was tailored by applying a sustainable chemistry and ILSS was improved with epoxy matrix via short beam shear strength measurement.

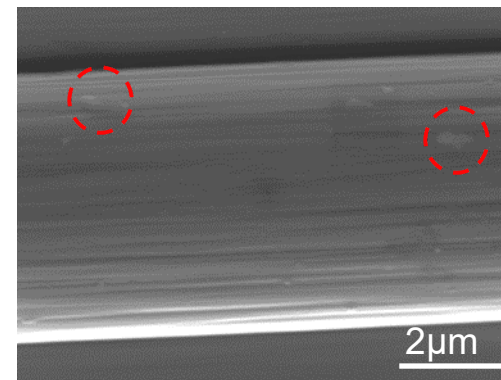


BS1: untreated carbon fiber  
BS2: commercial sized carbon fiber

Untreated CF

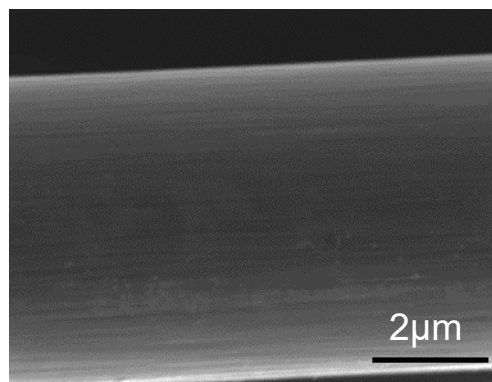


Commercial Sized CF

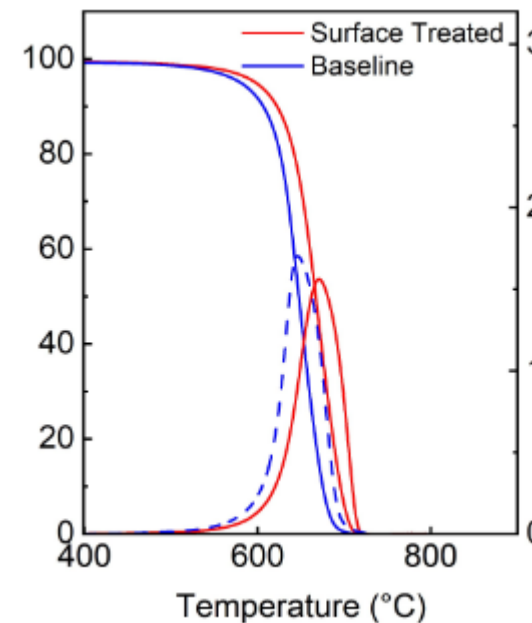


Agglomerates exist in commercial coating

Tailored CF



Well-dispersed thin polymer coating



The surface modification also enhanced the thermal stability

# Collaboration and Coordination

- Track 1 Focus on Higher TRL Precursor and Advanced Conversion
  - Felix Paulauskas, Bob Norris
  - Acrylic precursor suppliers interested in expanding markets
  - Advanced conversion partner 4XT/4M (co-inventors with ORNL)
- Track 2 Focus on Low TRL Advanced Precursor and Conversion
  - Logan Kearney, Mike Toomey, Shin Zhou, Amit Naskar
  - Precursor synthesis and processing to fibers
  - High throughput conversion of fibers made in house
- Cross-Cutting Activities
  - All Above Team Members – expanding precursor development, precursor scale-up, and conversion/post treatment activities
  - ORNL – David McConnell, Conversion of precursor fibers to CF
  - PNNL – Kevin Simmons and Yao Qiao – pressure vessel manufacturing cost and performance modeling
  - Tank Manufacturer(s) - TBD

# Remaining Challenges and Barriers

- ❑ Development of highly ordered PAN spun precursor fibers from low PDI precursor
  - ✓ High strength precursor fiber may help getting highly oriented high strength CF, but it imposes challenges with rapid conversion. We have high mechanical property goal with precursor fibers, but it may not be necessary.
- ❑ Multiple fiber handling during small scale stabilization and conversion can lead to damage in fiber surface. We will aim minimizing number of steps in stabilization. Thanks to other EERE investment, we will install a new robust fiber spinning line soon.
  - ✓ Low-diameter CF can improve mechanical properties but that may lower manufacturing throughput in a plant.
- ❑ Conventional conversion may not offer low-cost remedy unless CF properties are very high
- ❑ Translation of fiber properties to composite
  - ✓ Interfacial engineering

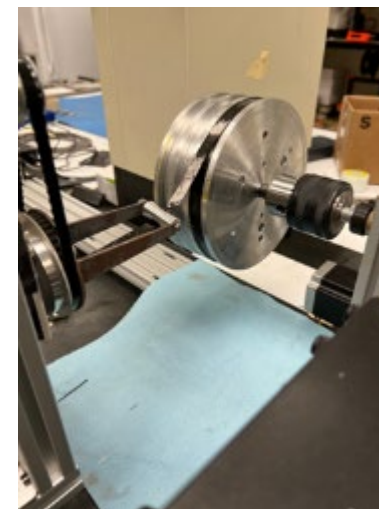
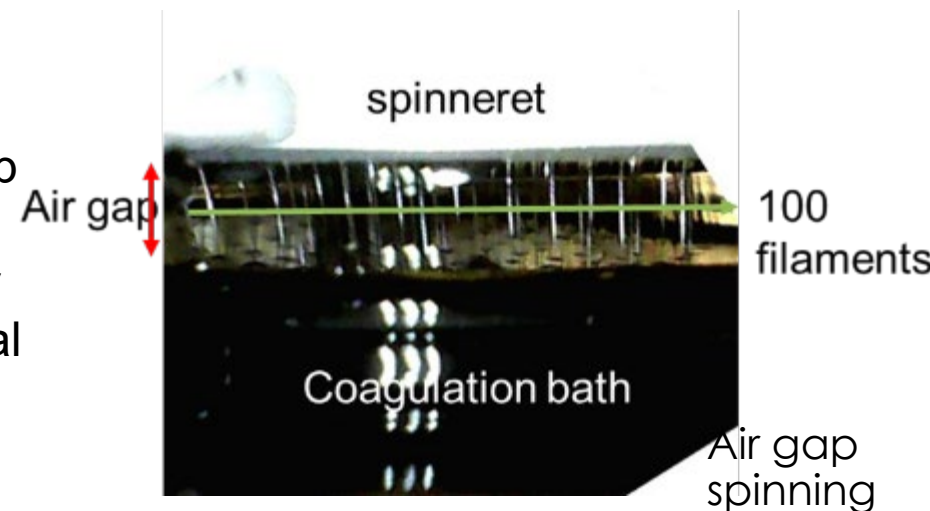
# Proposed Future Work

Current limitations to in-house wet spinning is driving the need for air-gap spinning

- Air gap spinning successfully established using commercial precursor powder, enables improved structure through higher loading (lower final porosity), increased chain alignment

Investigate cost savings areas

- Increased monomer conversion efficiency (less waste, more \$ efficient)
- Determined best solvent (DMSO) for highest processability relative to required processing energy
- Established terpolymer composition which facilitates processability, while lowering cyclization temperatures with comonomer and accelerant
- Established pathways to further reduce cyclization energy barriers through DFT simulation
- Developed stable air-gap spinning protocol for commercial polymer, optimizing for terpolymer



Ring test tooling for fiber strength measurement

Go/No-go milestone	Go/No-go based on CF performance achieving tensile strength >700ksi in tows of at least 100 filaments and length at least 100m	Carbon fiber properties tested by single filament mechanical characterization meets the property goal,	12/31/2022
--------------------	--	--	------------

# FY 2023 Milestone Status

Milestone Description	End Date	Type	
Delivery of a pre-cyclized precursor with 80 ksi tensile strength in 100 filament experimental tow.	9/30/22	Regular	Complete
Down-selection of preferred post treatment approach based on ILSS >12 ksi	12/31/2022	Regular	Complete
Textile and/or advanced precursor approach demonstrated to achieve 650ksi	3/31/2023	Regular	Complete
Go/No-go based on CF performance achieving tensile strength >700ksi in tows of at least 100 filaments and length at least 100m	6/30/2023	G/NG	
“Optimum” fiber diameter chosen, and updated fiber cost models reported. Projected cost data \$15/kg CF is validated.	9/30/2023	Regular	
Fiber Scale-up approaches for textile and advanced precursor reported and demonstration of 700 ksi tensile strength in scaled-up CF manufacturing.	12/31/2023	Regular	
Tank optimization model results completed and briefed	3/31/2022	Regular	
Final report draft completed and delivered	6/30/2024	Regular	

# Response to Reviewer's Comments

No comments received

# Summary

- Comprehensive multi-faceted approach established to assess:
  - Near-term methodology for modifying textile precursor approach for significant CF performance enhancement while retaining inherent textile cost advantages (Thrust 1)
  - Longer term precise molecular architecture, high throughput cyclization and formation of high-strength carbonized filaments with controlled morphology for CF performance at lower cost (Thrust 2)
  - Advanced conversion, post treatment, and tank design optimization applied to Thrusts 1 and 2 in (Cross-Cutting) analyses
- Portions of this work may be available to support industry-led projects down-stream
- Recently demonstrated 150 kDa PAN precursor molecular weight specifically for this project. The polymer showed <1.8 PDI and an air-gap spinning methodology is being developed for making extensible yet highly oriented precursor fiber.
- Recently demonstrated that alternative textile equivalent acrylic precursor was able to meet key milestone for achieving 600ksi tensile strength in single filament testing while also utilizing the advanced oxidative stabilization process. *(Industry standard impregnated strand data is typically 8-10% higher than average single filament data meaning we are rapidly approaching project performance target of 700ksi.)*
- Developing path for enhanced interfacial interaction between fiber and epoxy matrix.

Thank you!

# Technical Back Up Slides

# Thrust 1—Accomplishments and Progress: Other Tools in Thrust 1 Toolbox Also Support Thrust 2

- In related projects, we have achieved very good properties with textile precursors.
- We have attracted interest from textile producers in working towards goals of bridging key factors previously identified and optimizing towards goals of this initiative.
- This team has demonstrated capability to achieve equivalent or better performance via utilization of larger diameters and/or advanced conversion technologies to drive cost down

**Table 1. APO production of various diameter precursor.**

Oxidation Method	OPF Density (g/cc)	OPF Diameter (µm)	Oxidation Time (min)
Conventional	1.36	11	60-90
Plasma Oxidation	1.36	11	20
	1.36	16	50*
	1.36	20	84*

\*Results from testing with an experimental textile-grade PAN precursor.

**Table 2. Performance of APO Precursor after Full Conversion.**

Oxidation Method	Data Source	Tensile Strength (ksi)	Tensile Modulus (Msi)	Oxidation Time (min)
Conventional	Mfr. Website*	580	35	60-90**
Plasma	Average (CFTF)	660	36.5	20
	Minimum (CFTF)	640	36	

\*These values are published by the CF manufacturer.



# Summary Thrust 1

- In spite of partner setbacks, near-term methodology for modifying textile precursor approach demonstrates significant CF performance enhancement while retaining inherent textile cost advantages
- APO processing yields equivalent or better properties for this high performance fiber at more rapid conversion rates for cost savings
- Work still in progress on optimizing properties from contracted precursor formulation/spinning development to compare against other candidates
- Next steps are to project properties and cost for tank studies
- Portions of this work may be available to support industry-led projects down-stream
- Also working with another potential textile precursor supplier, but their current product forms are not expected to be competitive with property targets without additional development

# Project Accomplishments

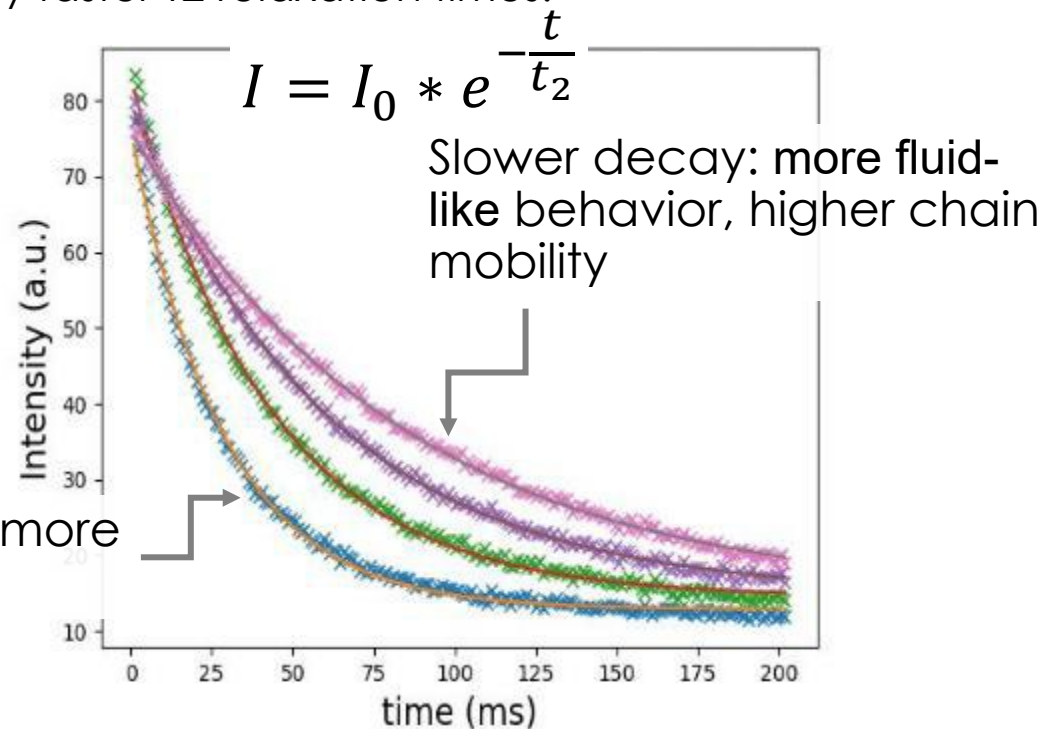
- Recently demonstrated 150 kDa PAN precursor molecular weight for new precursor developed specifically for this project. The polymer showed <1.8 PDI and an air-gap spinning methodology is being developed for making extensible yet highly oriented PAN precursor fiber.
- Acquired baseline textile-based precursor having >10% elongation. Completed characterization of this precursor and initial processing conditions identified; oxidized fiber delivers desired density
- **Recently demonstrated that alternative textile equivalent acrylic precursor was able to meet key milestone for achieving 600ksi tensile strength in single filament testing while also utilizing the advanced oxidative stabilization process.** (*Industry standard impregnated strand data is typically 8-10% higher than average single filament data meaning we are rapidly approaching project performance target of 700ksi.*)
- Developing path for enhanced interfacial interaction between fiber and epoxy matrix.

# Low field NMR for probing polymer-solvent, polymer-polymer interactions

**With respect to comonomer selection, what solvent-polymer pairs are optimal?  
How does polymer loading influence chain mobility?**

Low-field T2 relaxation probes sub-chain movement/mobility and is inversely proportional to dipolar coupling constants in solution state.

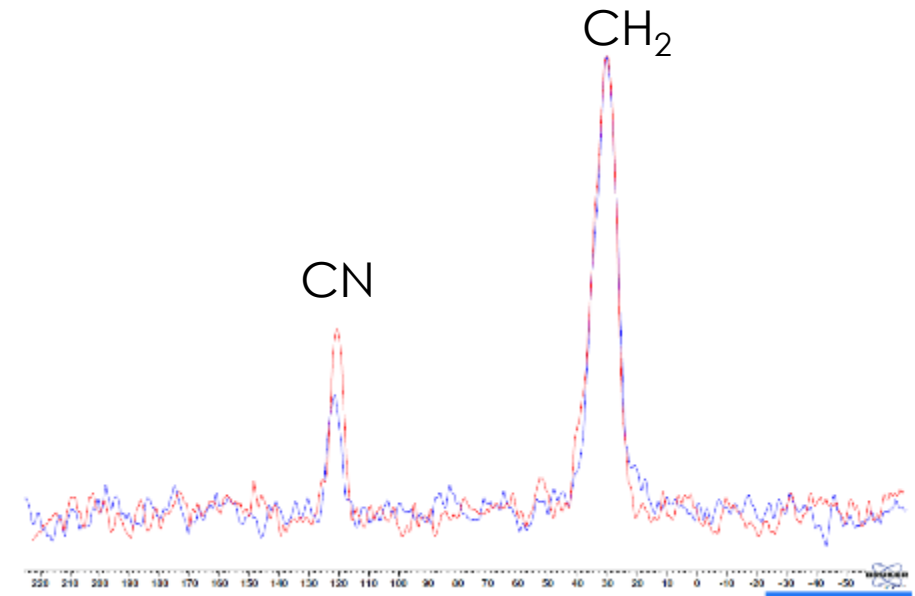
- more rigid behavior (e.g., stiffer chains, high dipolar coupling, shown by faster T2 relaxation times).



Fit with exponential decay function to find T2

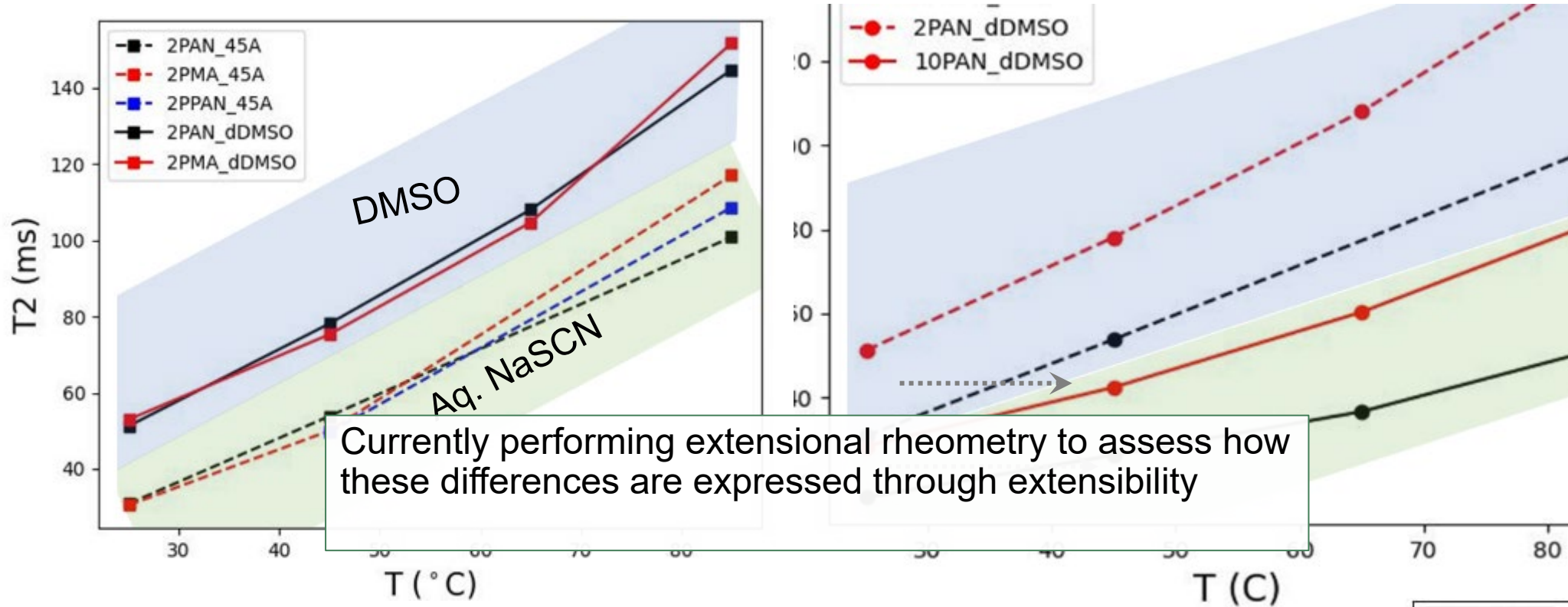
Faster decay: more rigid behavior

High-field NMR to probe CN rotation after fiber spinning

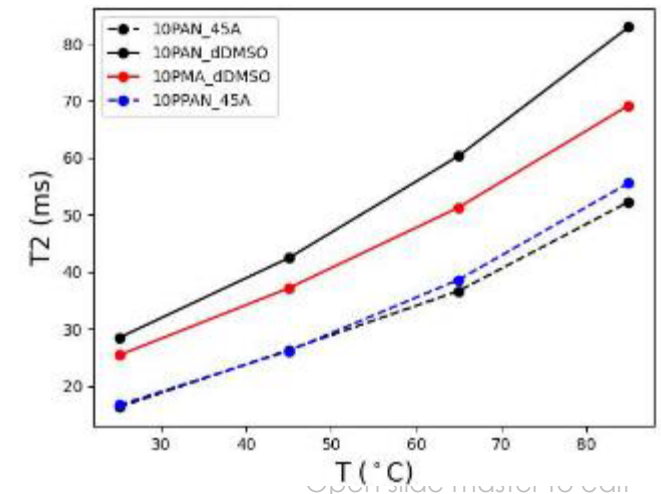


1.2 s exchange showing bond rotations

# Rheological implications based on polymer-solvent interactions

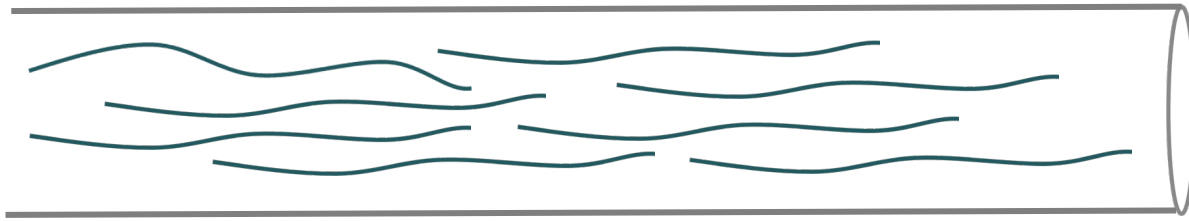
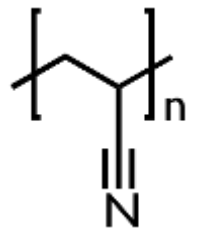


While aqueous processing of precursor may be more environmentally friendly, they produce dopes with worse chain mobility (not beneficial to processability)



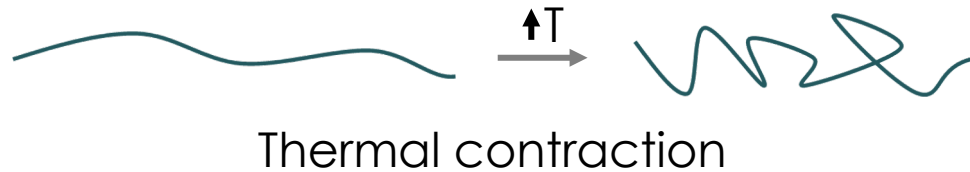
1. G. Santhana Krishnan<sup>a</sup>, P. Thomas<sup>b</sup> and N. Murali<sup>c</sup>

# Mechanochemical influences on PAN-based carbon fibers

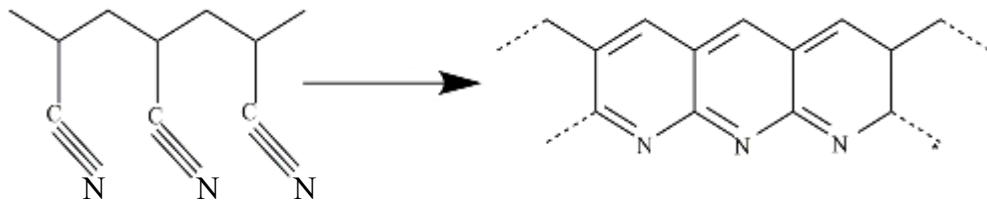


Idealized PAN based CF precursor having high degree of initial molecular chain alignment

## Competing Phenomena

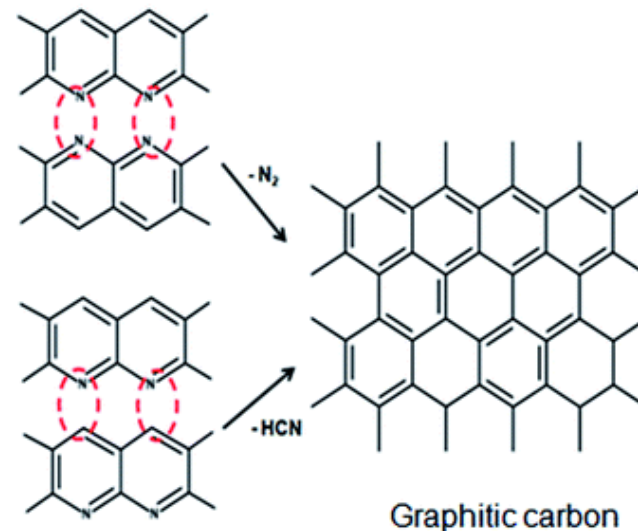


## Stabilization

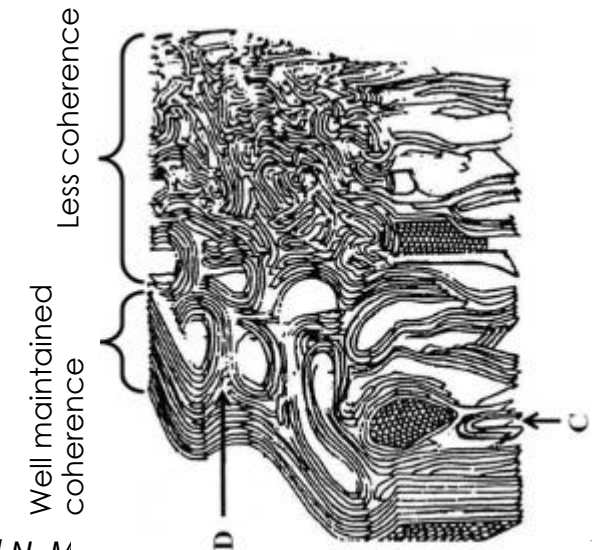


Cyclization reaction facilitated by conformational freedom

## Carbonization



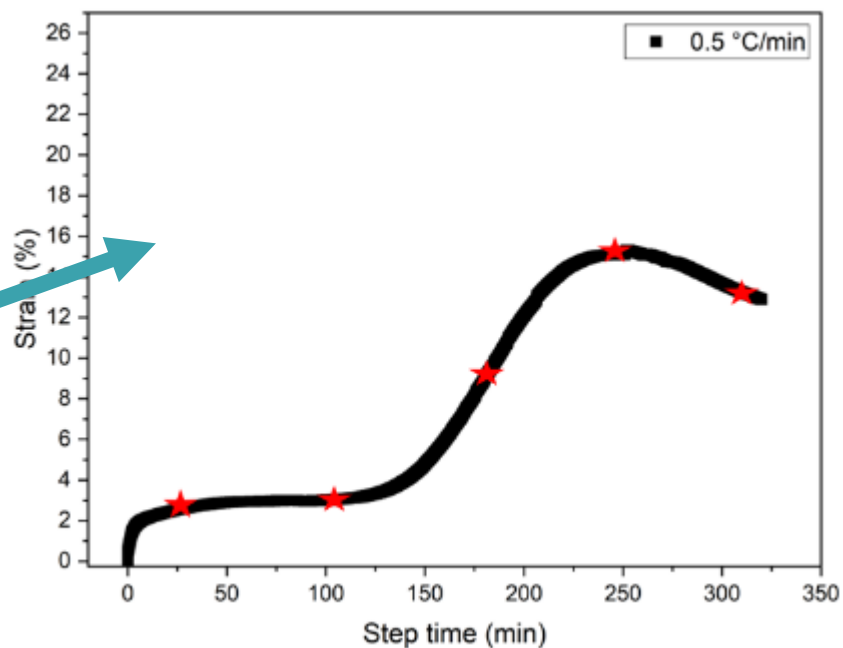
## CF structure



# Mechanochemical evaluation

Once precursor fiber form, how does as-received processing history (draw ratio, diameter, etc.) influence oxidation? What considerations must be made given processing history, chemistry?

How does thermal processing under constant force conditions influence cyclization and structure maintenance/development?



What alterations to mechanochemical phenomena occur when comonomers are incorporated?

How does variation in initial structure alter mechanochemical phenomena?

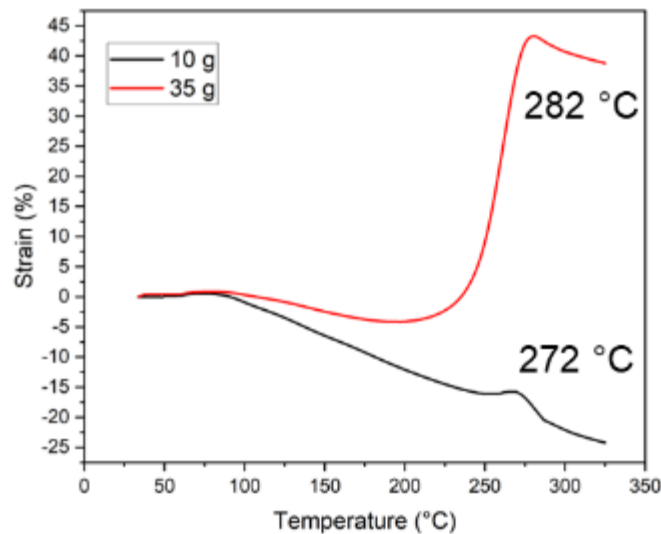
RSA (high sensitivity DMA) enables rapid process optimization at mg scale while a high degree of temperature control allows for characterization of characteristic transitions in the material throughout the process.

# Mechanochemical influences on PAN-based carbon fibers

**CF precursors commonly have comonomers which lower  $T_g$  and/or accelerate cyclization.**

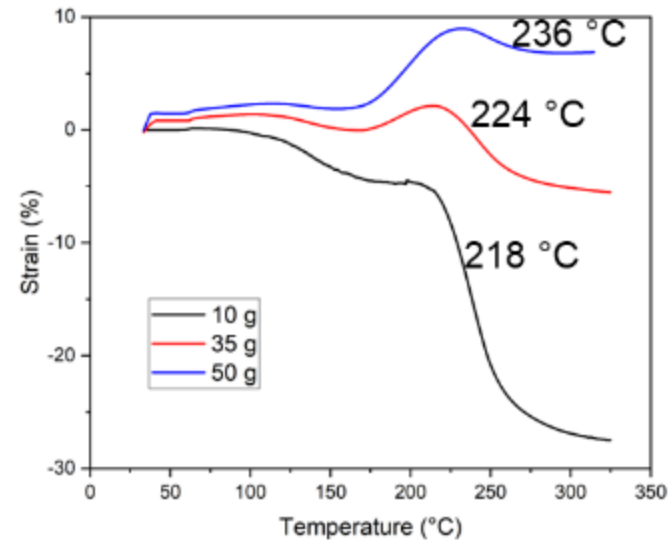
- *How do these incorporations, in combination with mechanochemical considerations affect processing?*

PAN copolymer, unaccelerated



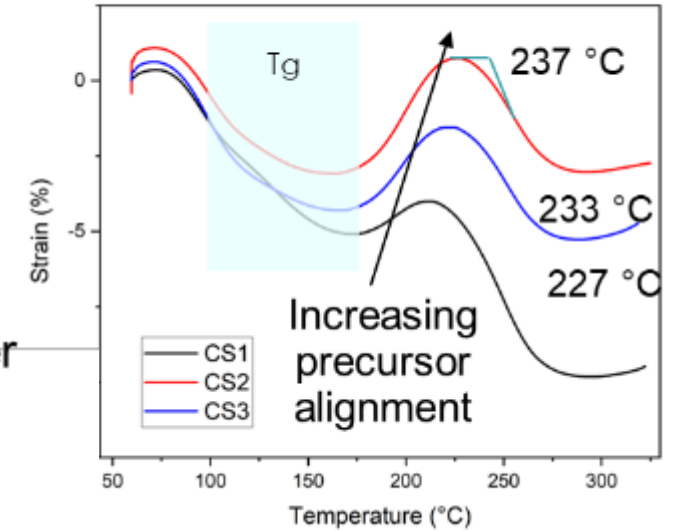
Largest window for stretching, though tendency to burn during oxidation

Accelerated PAN terpolymer



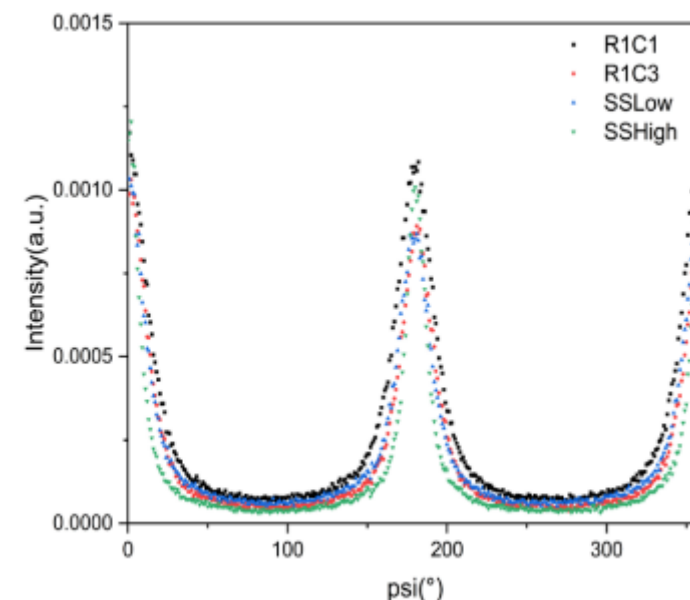
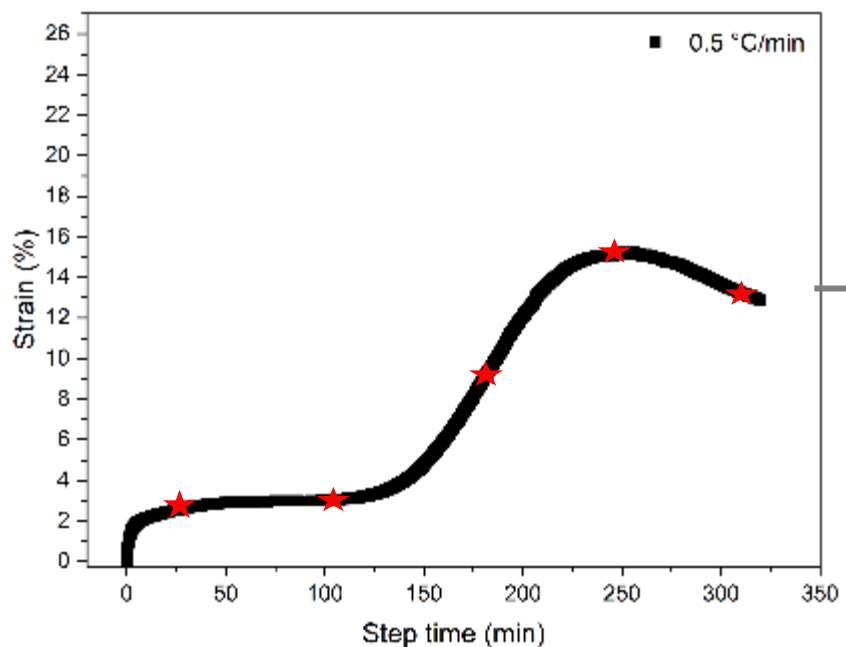
Lower oxidation temp., higher need for alignment prior to oxidation

Effect of initial alignment



# Next steps:

- Chemical, structural characterization at various points throughout the process (SAXS)
- Connect to DFT
- Continued RSA characterization with homoPAN



# Polyacrylonitrile (PAN): Cyclization and beyond

## ***First step: Perspective from the ab initio (DFT) approach at a small length scales***

- **Long standing problem—**

### **What is known:**

- PAN cannot cyclize on its own
- Free electron needed to initialize cyclization
- High temperature needed

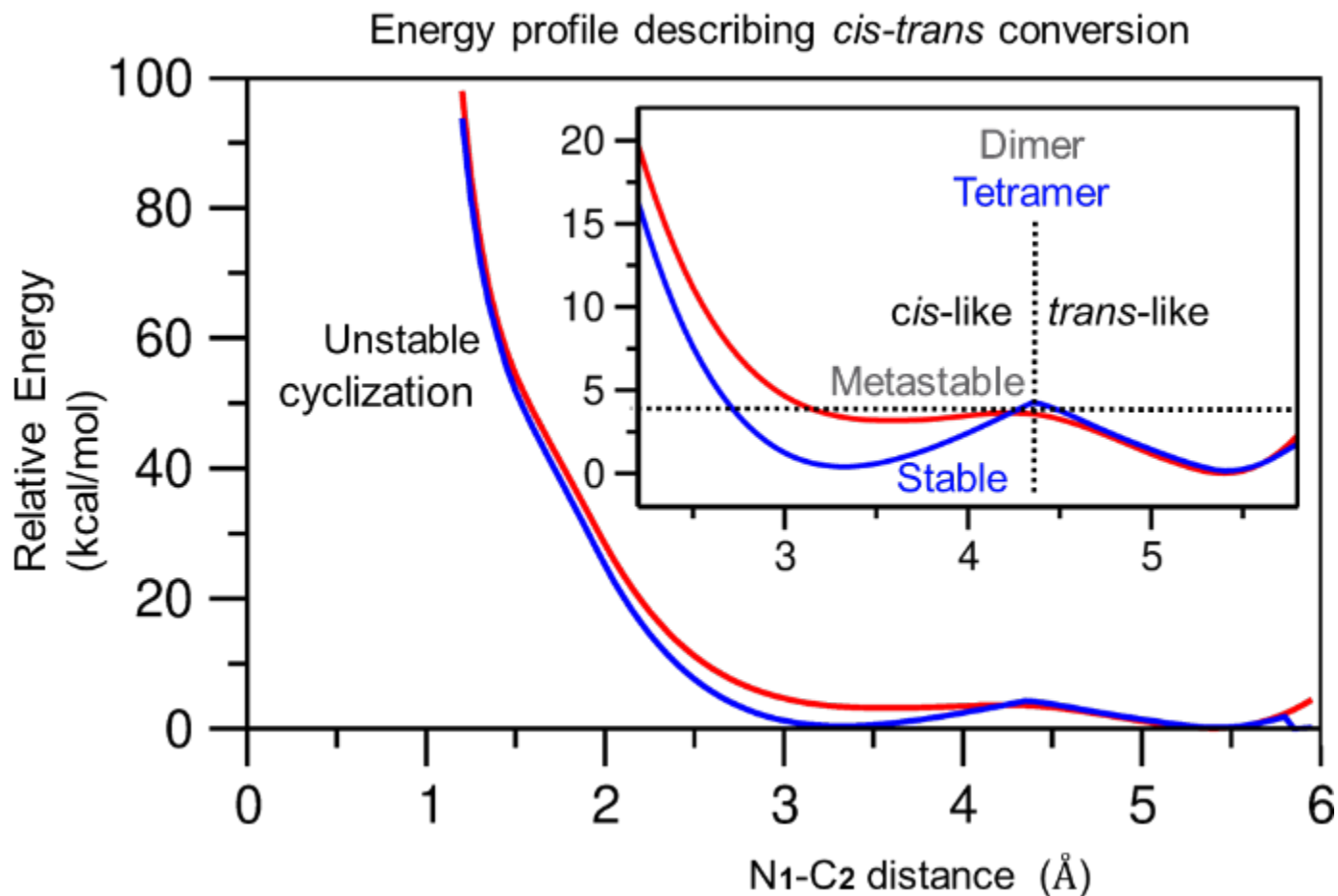
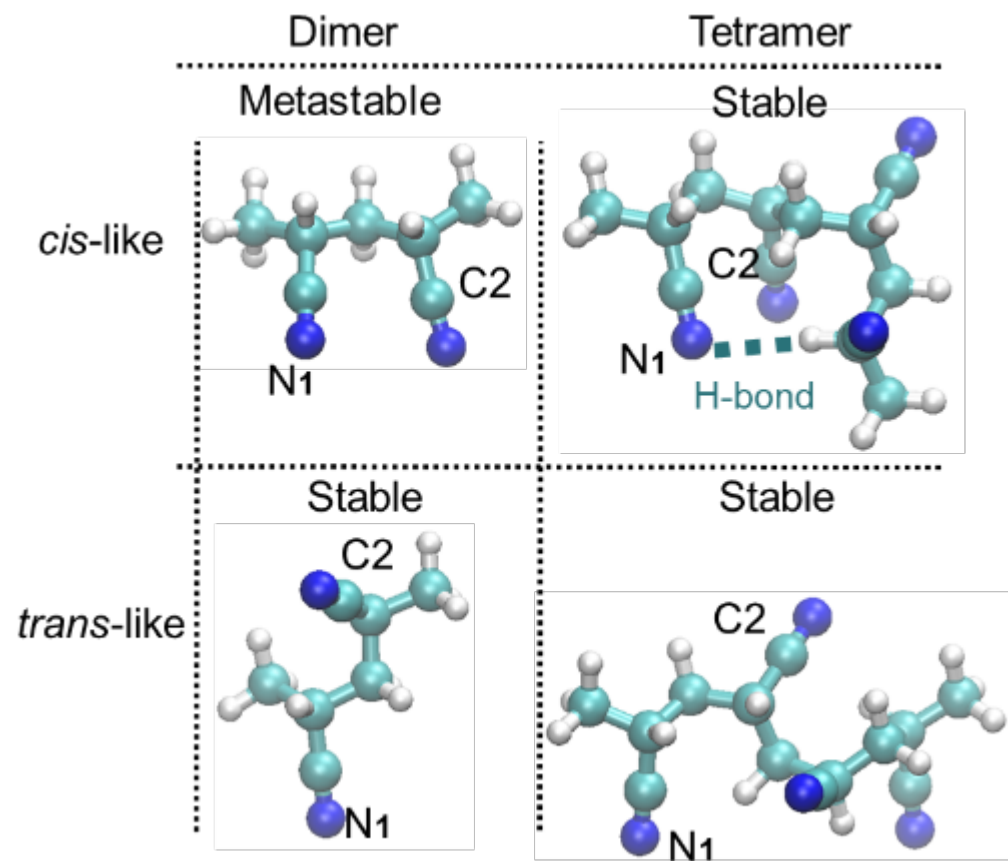
### **What can be done—**

- Quantify cyclization—can we determine and optimize energy required for cyclization?  
What are the roles of entropy/enthalpy ?
- Which electron carrier (radical) or negatively charged ions will do a better job?
- Can we access structurally unique multiple metastable/stable states in the cyclization process that can be functionalized to achieve desired/tailored properties such as ion transport? Can we avoid structural artifacts?
- Does PAN becomes more rigid when cyclized, if so, can we quantify the bond length and strength as going from fully extended to cyclized structures?

## ***Second step: Leverage the understanding of PAN cyclization and carbon structure evolution using accurate and efficient Neural Network Interatomic Potentials***

# Understanding from Ab-initio Simulations for PAN bare configurations: Dimer vs Tetramer

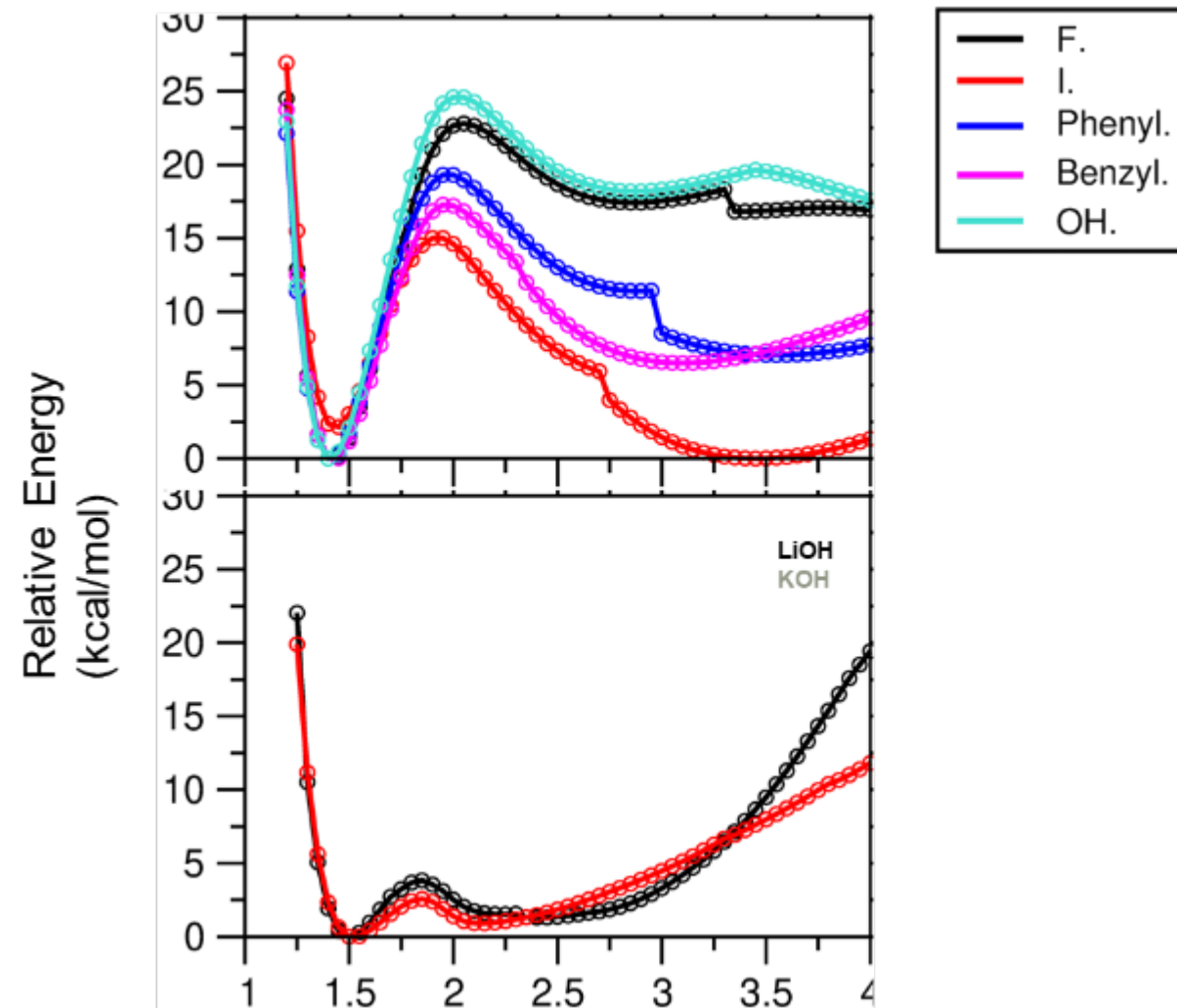
- Cyclization not possible—energetically unstable
  - *cis-trans* conversion—possible (Energy barrier ~ 4 cal/mol)



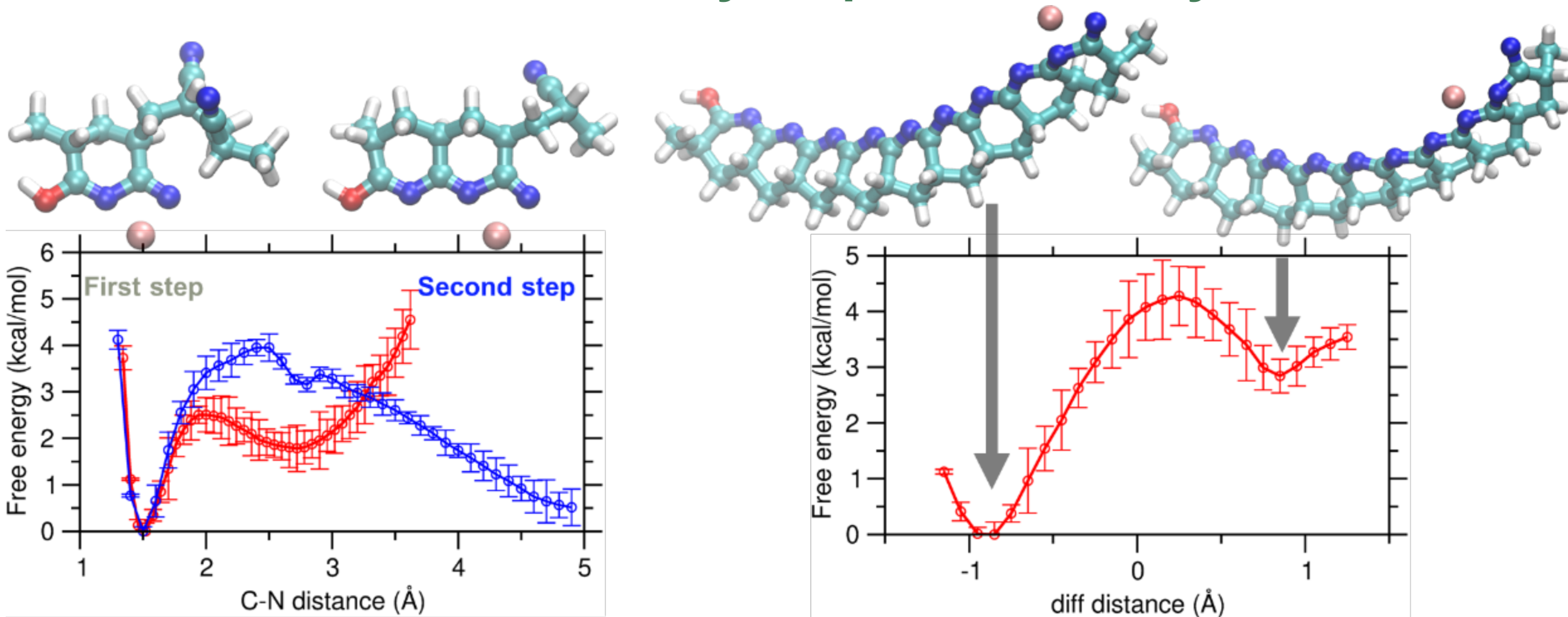
# Understanding from Ab-initio Simulation on Initialization of PAN cyclization with radicals

Each radical attach to C1 (C of first CN) is unique, allowing

1. Different stabilization of initially cyclized structure
2. Tunability of functionalization and cyclization using various accelerants



# Ab-initio Simulations to Study Sequential PAN cyclization



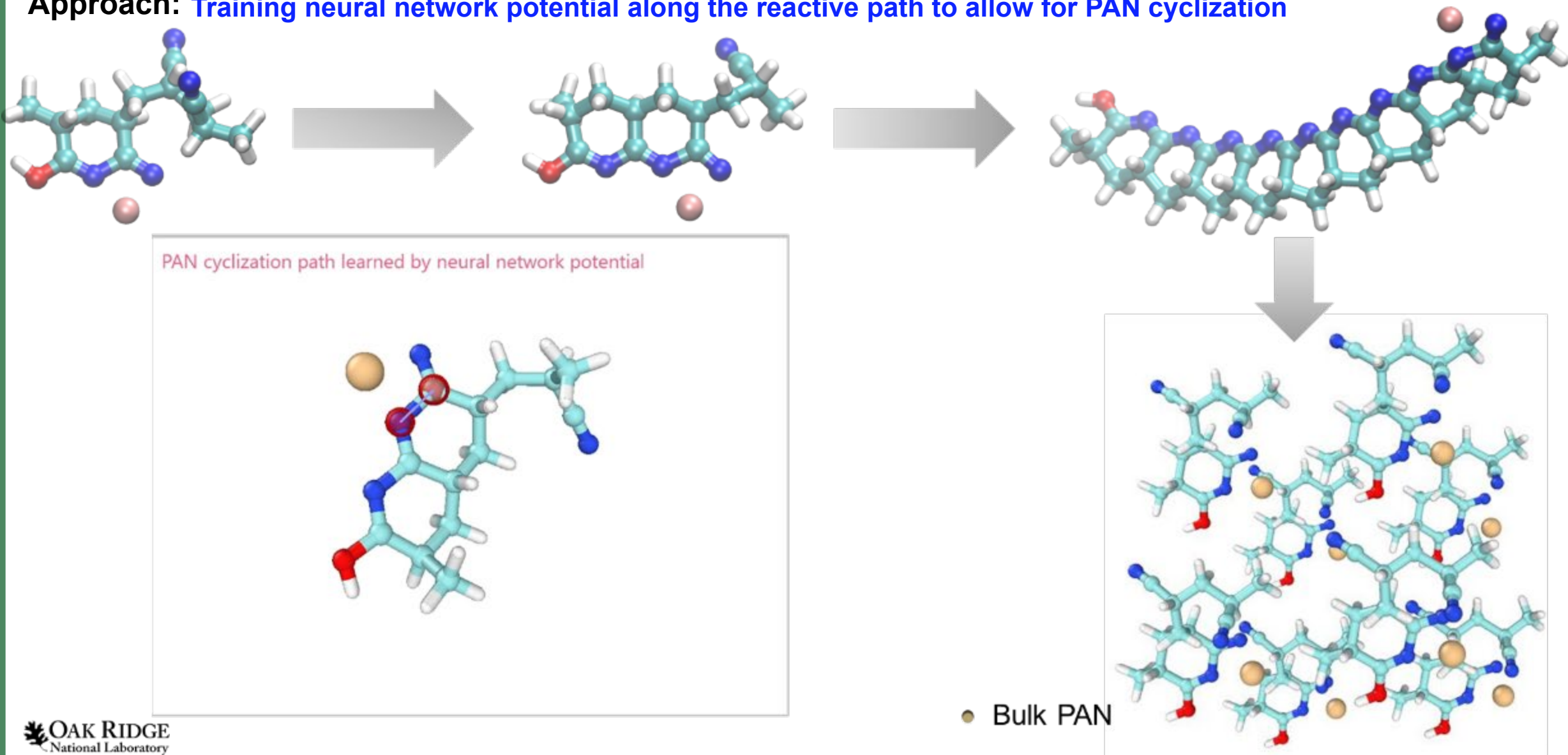
Umbrella sampling dynamics Dynamics showed:

1. Critical steps—initialization and sequential cyclization
2. 3-step and 9-step cyclization both indicating ion to be located near the last cyclized unit

*Due to inefficiency of Ab-initio calculations, it is challenging to study the cyclization for larger PAN chains → Train an efficient and accurate neural network potential*

# Understanding PAN cyclization at large length scales

Approach: Training neural network potential along the reactive path to allow for PAN cyclization



# Investigating solvent effects on PAN cyclization and ion transport

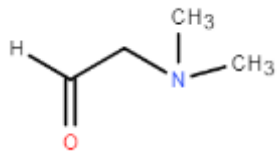
## Approach:

Efficient and Accurate Neural Network Interatomic Potential will be developed by training on the ab-initio data for solvent, PAN-solvent

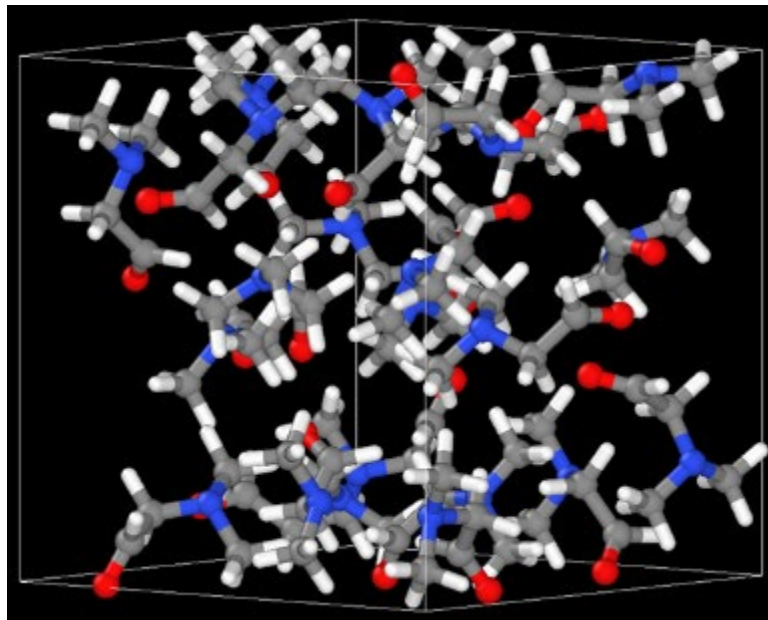
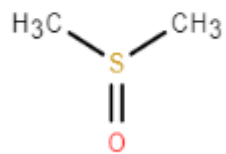
### Solvent:

Solvents to consider:

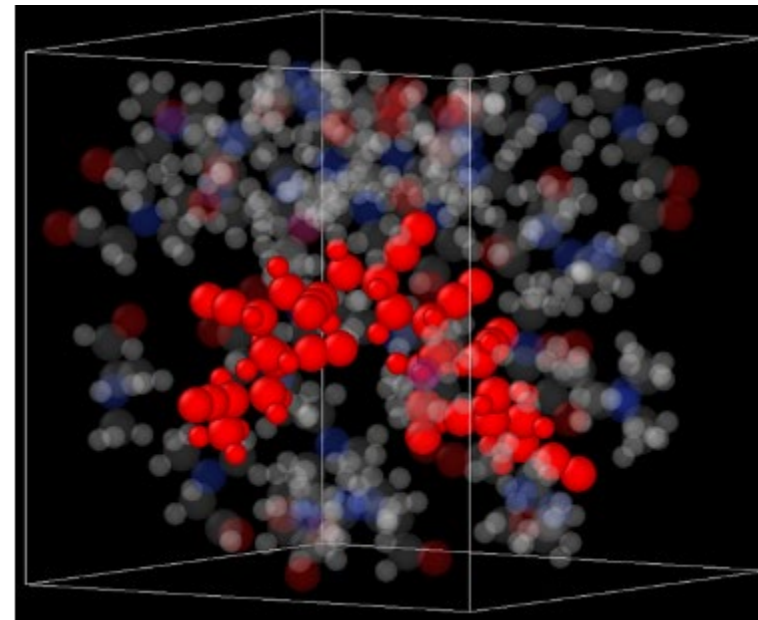
- DMF



- DMSO



### PAN chain in solvent:



PAN chain  
(molecular weight  
~ 550 g/mol)

# Processing and CF evaluation

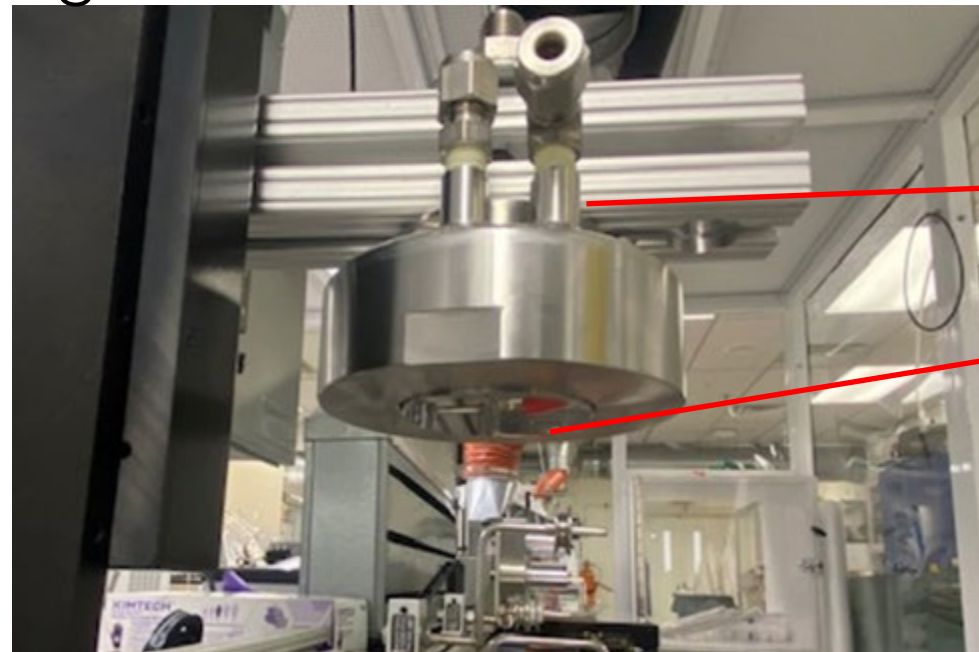
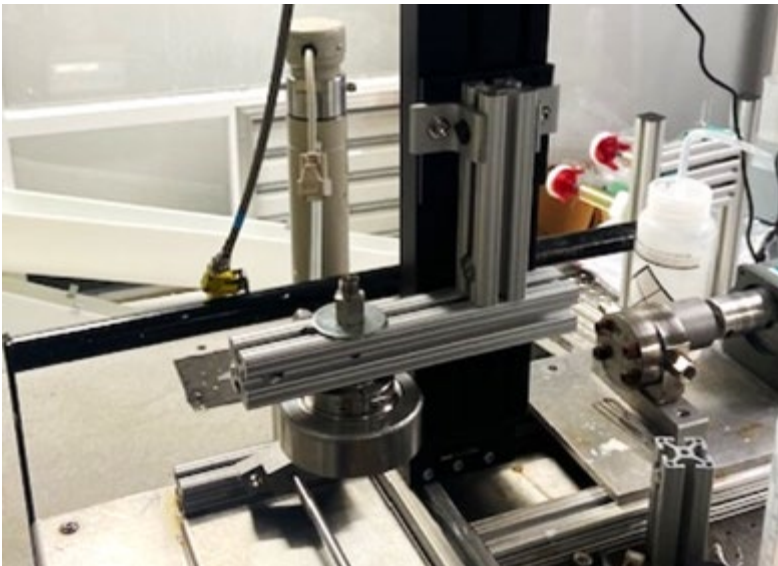


- New precursor formulations used in wet spinning of fibers with various draw ratios, residence times
- Various oxidation conditions (temp, ramp, stretch) used to reach target density
- Various conversion protocols used to reach final carbon structure prior to single filament testing

# Air Gap Spinning

- Current limitations to in-house wet spinning is driving the need for air-gap spinning
  - Air gap spinning successfully established using commercial precursor powder, enables improved structure through higher loading (lower final porosity), increased chain alignment

Bath-mounted air gap spinning setup with motorized z-stage



Heating/cooling jacket for precise control over rheology

500 hole spinneret of various L/D

# Technology Transfer Activity

The project is founded on prior set of IP in both high and low TRL Tracks. Those prior IPs are being considered for commercialization

- Paulauskas et al. US Patent 7,786,253 (2010); 9,447,205 (2016)
- U.S. Patent No. 10,407,802 (2019); 10,961,642 (2021)
- Naskar AK, Jackson CD. Method of Producing Carbon Fibers from Multipurpose Commercial Fibers. U.S. Patent No. 10,961,642 (March 30, 2021).
- Jackson CD, Naskar AK. Method of Producing Carbon Fibers from Multipurpose Commercial Fibers. U.S. Patent No. 10,407,802 (September 10, 2019).

New set of IP is being developed.

Naskar AK, Yu Z, Zhou X, Bowland CC. Improving Interfacial Properties of Carbon Fiber-Reinforced Epoxy Matrix Composites, US Provisional Patent Application No. 63/432,429 (filed on December 14, 2022) (ORNL ID 5151).

# Publications and Presentations

Naskar AK. “Carbon Fiber Development for Pressure Vessels”, 2nd Annual Materials Innovation and Advanced Technology Leadership Forum, SAMPE Composite in Hydrogen World, Huntington Beach, CA, January 25, 2023.

Naskar AK. “Carbon Fiber and Composite Manufacturing for Hydrogen Storage Tanks”, Manufacturing Automation and Recycling for Clean Hydrogen Technologies Expert Meeting (H2-MACH; Virtual Meeting) Organized by US DOE, EERE-HFTO (May 25, 2022).

Zhou X,\* Belianinov A, **Naskar AK**. Analyzing Carbon Fiber Structures Observed by Helium Ion Microscopy and their Mechanical Properties. *Carbon Trends* 4, 100055 (2021).