Synthesis, Thermal, and Rheological Evaluation of High C-Yield-Soluble Poly(phenylacetylene) Co-polymer Derivatives as New Carbon Fiber Precursors

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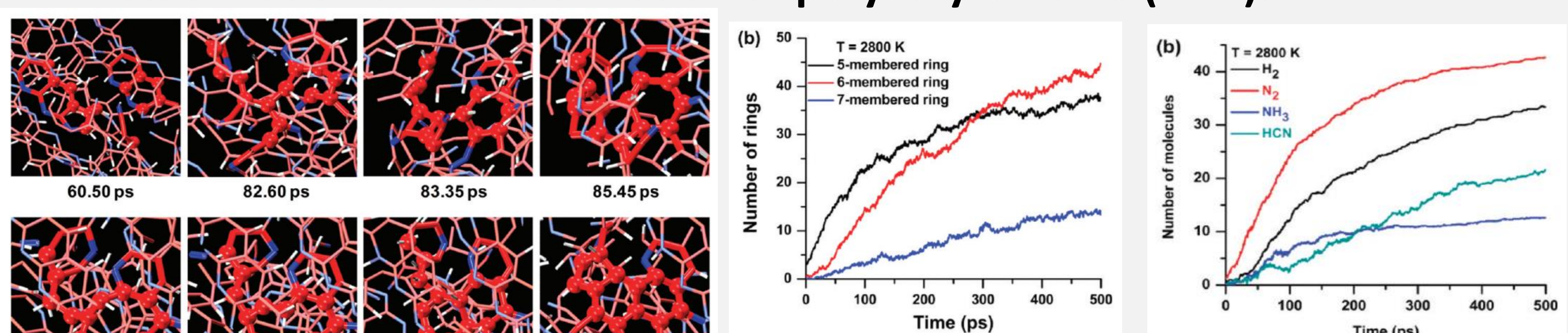
Introduction

- **ReaxFF** molecular dynamic simulations are used for observing stabilization and carbonization of **polyacrylonitrile (PAN).**



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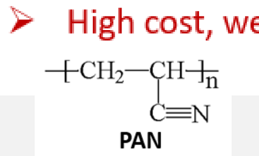
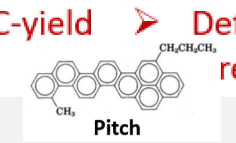
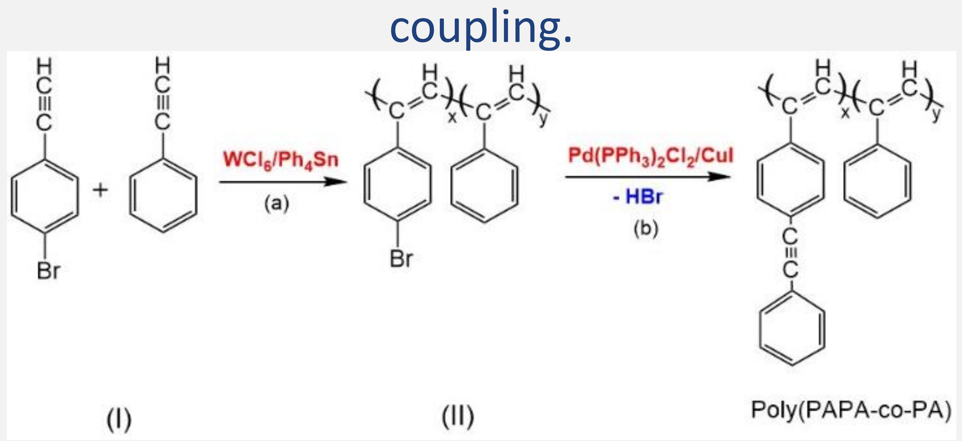
PAN precursor	Pitch precursor
Advantages:	Advantages:
- Tension during thermal conversion	- Low cost, melt spinning, 70% C-yield
- Low defects, good alignment, high tensile strength	- High elastic modulus
Disadvantages:	Disadvantages:
- High cost, wet-spinning, 50% C-yield	- No tension for thermal conversion
	- Defects, poor alignment, low tensile strength





Synthesis of Precursors

Schematic 1. Synthetic route to prepare poly(PAPA-co-PA) via (a) Metathesis (Ziegler-Natta) copolymerization and (b) sonogashira coupling.



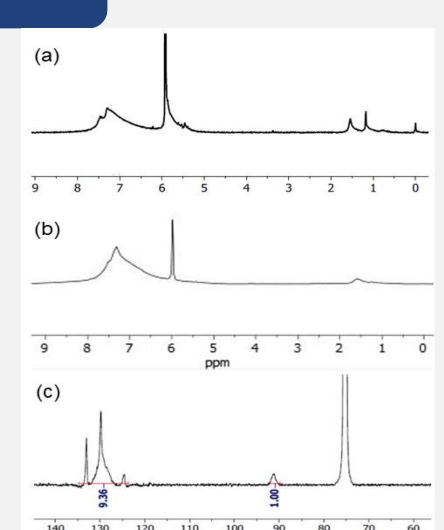


Figure 1. ^{1}H NMR spectra of (a) poly(4BrPa-co-PA) and (b) poly(PAPA-co-PA). ^{13}C NMR of poly(PAPA-co-PA) (c) all in 1:1.

Thermal Analysis Results

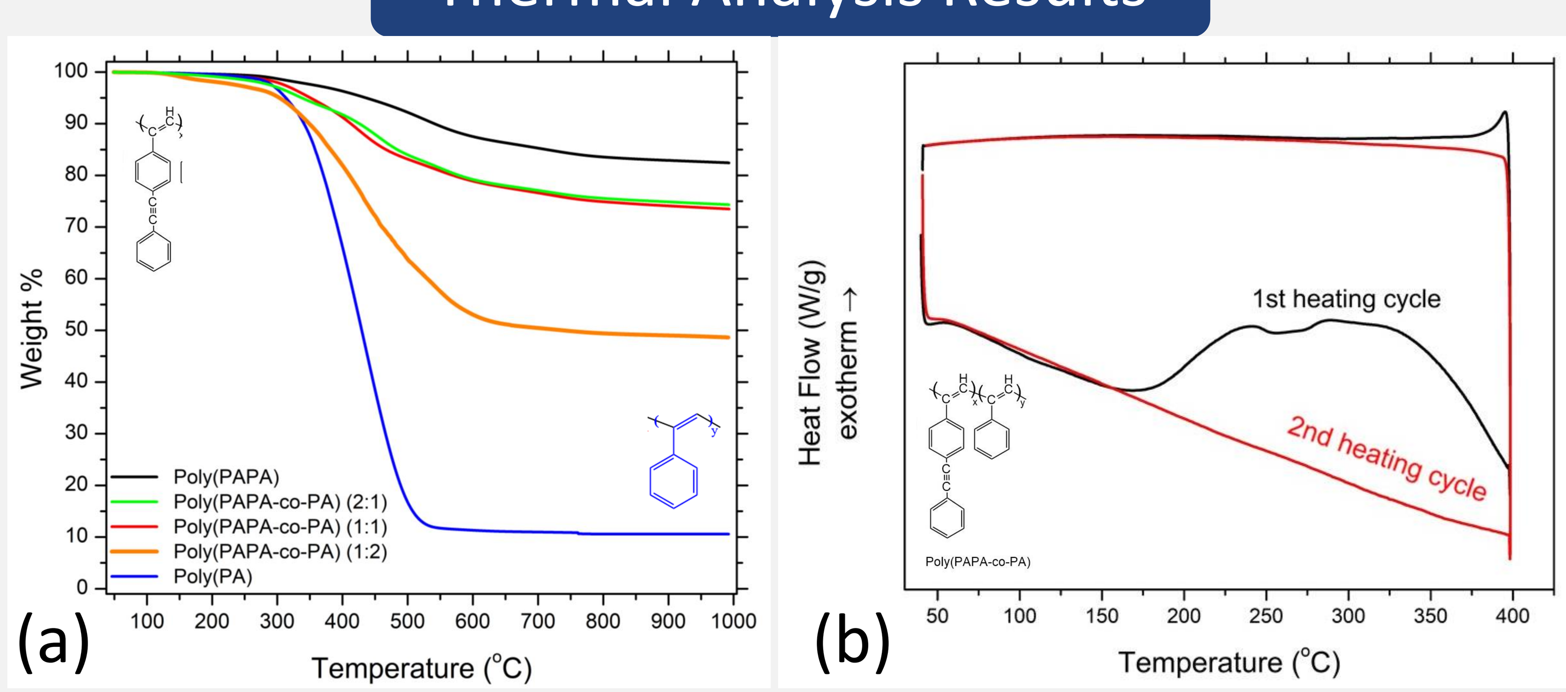
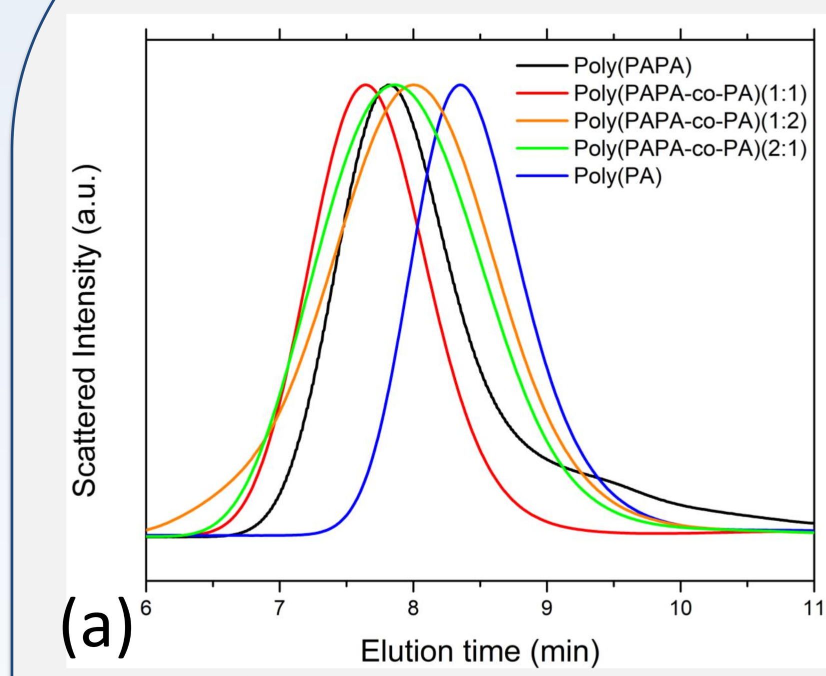


Figure 2. (a) Dynamic TGA measurements in N_2 at 10 °C/min for poly(PA) and its derivatives and (b) DSC trace of poly(PAPA-co-PA) 1:1 also in N_2 at 10 °C/min.

- TGA shows non-linear relation of the composition and the C-yield, which allows for the opportunity to minimize cost and maximize C-yield.
- Exothermic peak observed 1st but not 2nd cycle, indicating cross-linking.

Molecular Weight Analysis



Precursor	Mw (kg/mol)	Mn (kg/mol)	PDI
Poly(PA)	50.0	23.0	1.97
1:2 Poly(PAPA-co-PA)	70.8	31.4	2.26
1:1 Poly(PAPA-co-PA)	217.0	111.0	1.97
2:1 Poly(PAPA-co-PA)	116.8	49.7	2.35
Poly(PAPA)	177.0	141.0	1.25

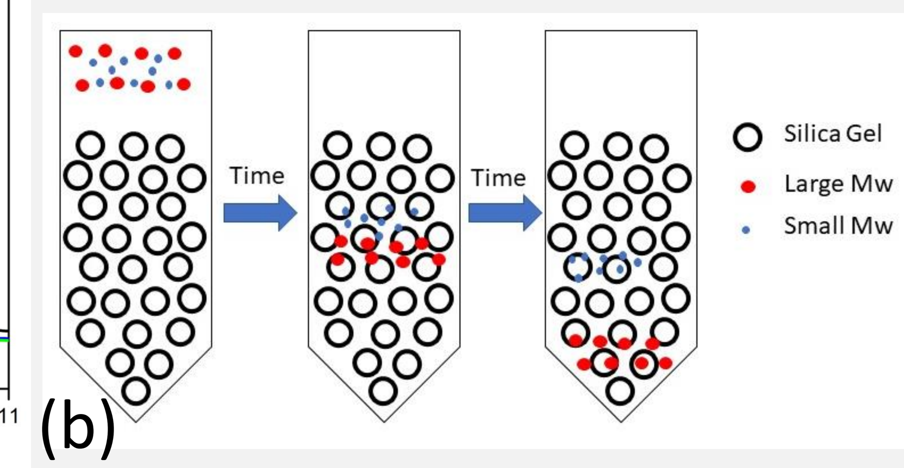


Figure 3. (a) Size exclusion chromatography (SEC) measurements of poly(PA) and its derivatives in THF at 25 °C. (b) Schematic of SEC methodology.

Analysis of Carbonized Precursors

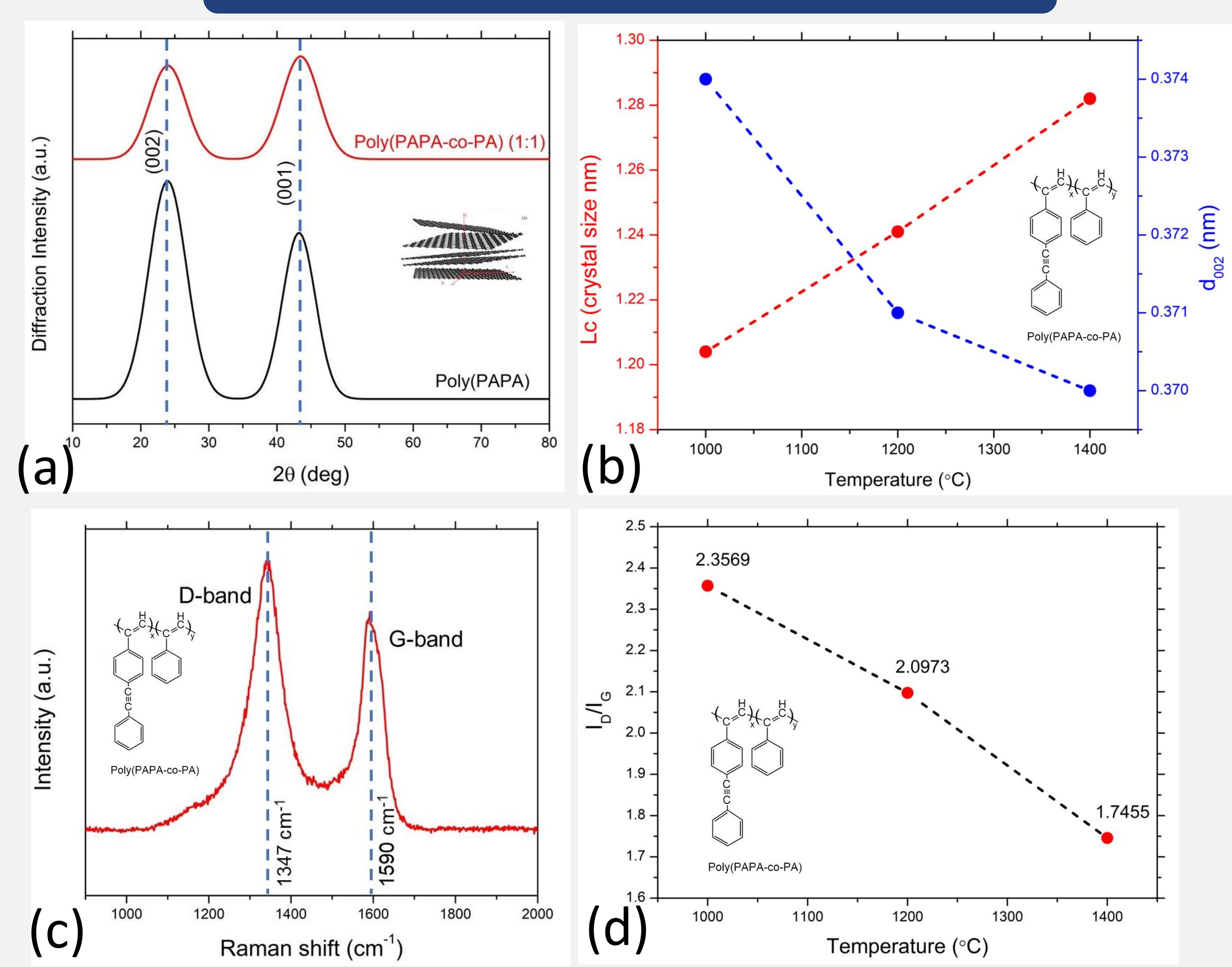


Figure 4. (a) 1D integrated XRD profiles for poly(PAPA-co-PA) and poly(PAPA) carbonized in argon at 1400 °C. (b) Crystal size and d-spacing trends with respect to increasing temperature for poly(PAPA-co-PA).(c) Raman spectra (λ = 514.5 nm) of poly(PAPA-co-PA) carbonized in argon at 1400 °C. (d) Intensity ratios of the D and G bands at corresponding temperatures for poly(PAPA-co-PA).

Rheological Characteristics

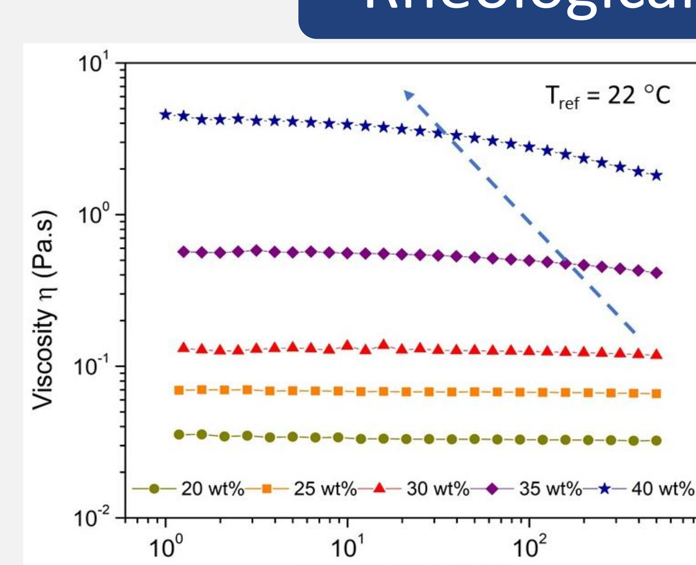


Figure 5. Concentration dependent flow sweep rheological behavior of poly(PAPA-co-PA) (1:1) in toluene at 22 °C.

- Arrow indicates the on-set of shear thinning, which is a requirement of wet or electrospinning
- Within desired zero-shear viscosity range for solutions w/ shear-thinning.

Microfiber Processing and Morphology

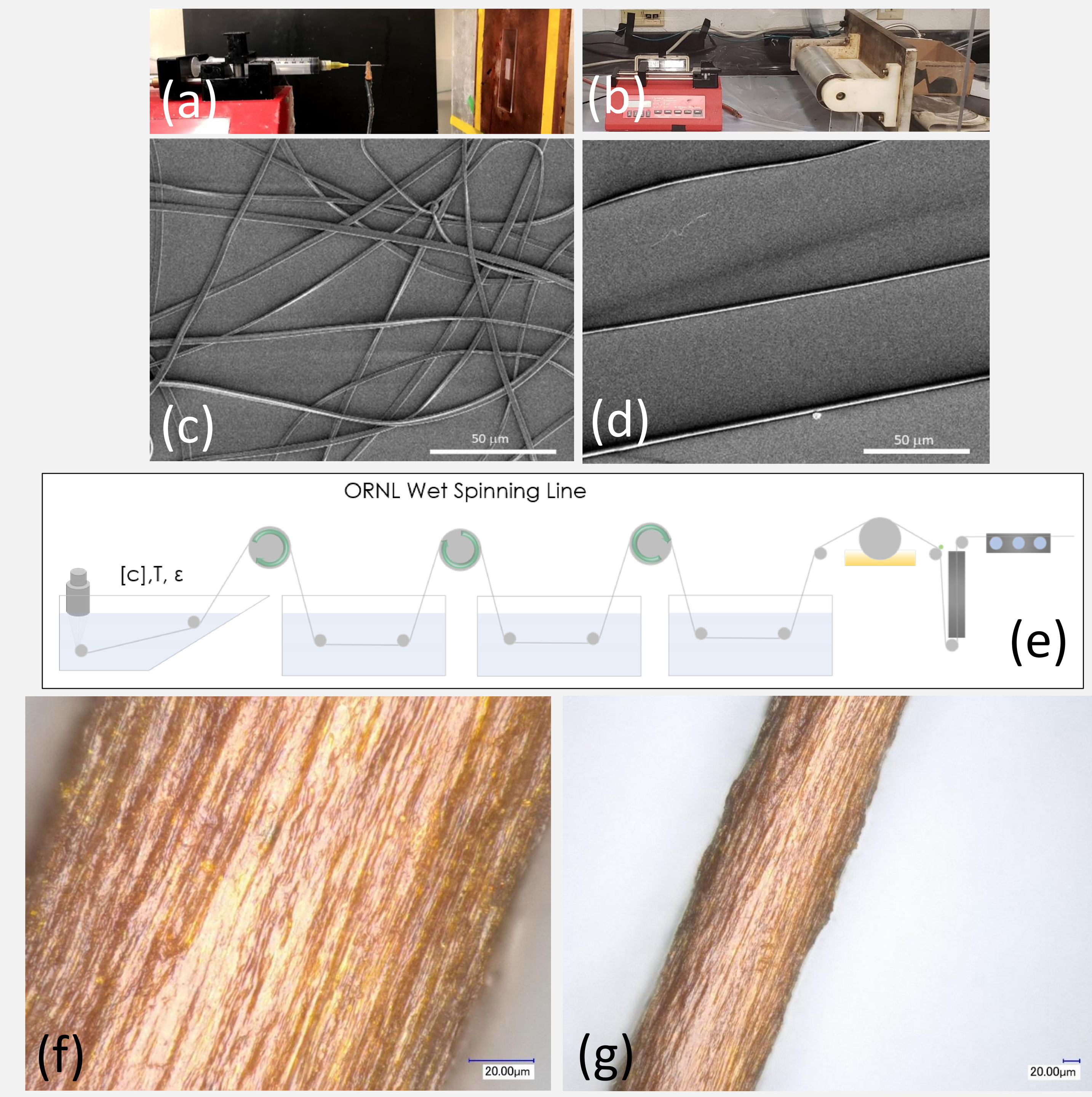


Figure 5. Depiction of electrospinning apparatus for (a) disordered and (b) aligned microfibers. SEM micrographs of iridium coated, (b) disordered (collected on flat glass slide) and (c) aligned poly(PAPA-co-PA) ~10 micron fibers from 35 wt% THF solution, 10 mL/hr flow rate, 15 kV, a distance of 30 cm, and onto a 15 cm diameter cylindrical drum at 10 RPM. (e) Schematic of ORNL wet-spinning apparatus. (f) and (g) Show optical micrographs of wet-spun poly(PAPA-co-PA) (~100 micron) fibers.

Conclusions / Future Work

- Measurements of TGA/DSC-MS to evaluate the molecules removed during the stabilization and carbonization.
- Reduction of fiber diameter and Mechanical properties of carbonized fibers are currently being tested and processed.

Acknowledgements & References

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