A New Approach to Synthetic Spider Silk: Gradual Coagulation of Complex Coacervates *via* Microfluidic Fiber Spinning

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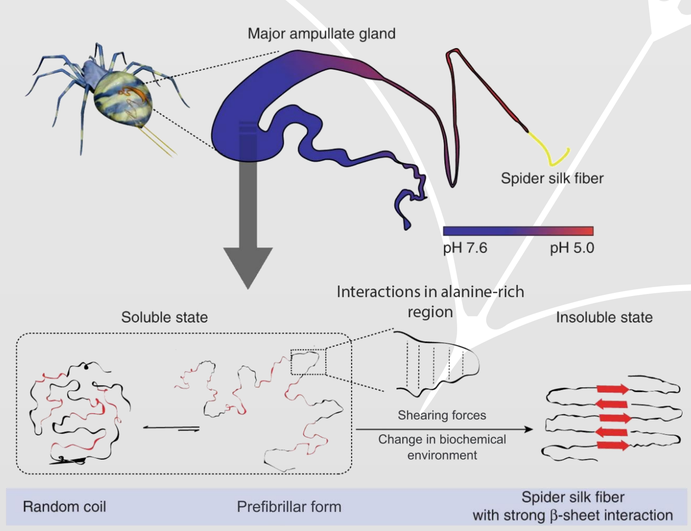
Introduction



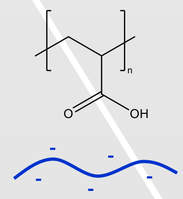
Proposed mechanism of β-sheet formation of spider dragline silk. Image adapted from [2].

Spider silk is renowned for its exceptional mechanical properties. Characterized by high extensibilities and tensile strengths of up to 1.6 GPa[1], it outperforms many man-made materials.

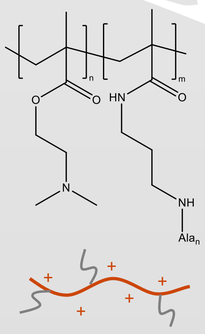
Spider silk proteins contain repetitive domains consisting of polyalanine-rich segments. The strength of spun fibers is in part attributed to the presence of these β-sheet forming regions. It is believed that gradual changes, such as in pH, shear or ionic strength, along the spider's spinning duct facilitate the α-helix to β-sheet transition of the protein.[2]

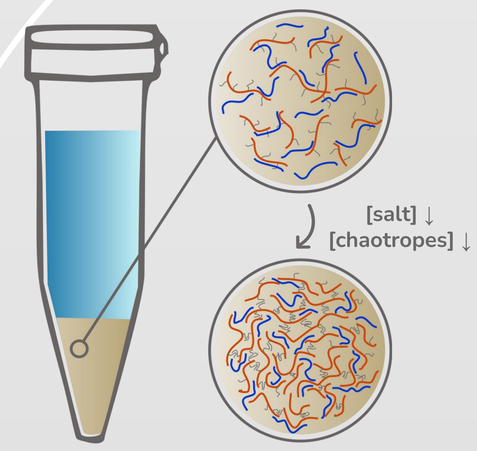
To study this natural processing system, we use a simplified spidroin-mimic by synthesizing polyelectrolytes poly(acrylic acid) (PAA) and alanine grafted poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA-Ala) and processing them to form a complex coacervate. Using microfluidics, we want to mimic the spinning duct by introducing gradients along the coagulation channel in which the liquid coacervate hardens into a fiber.

PAA



PDMAEMA-Ala

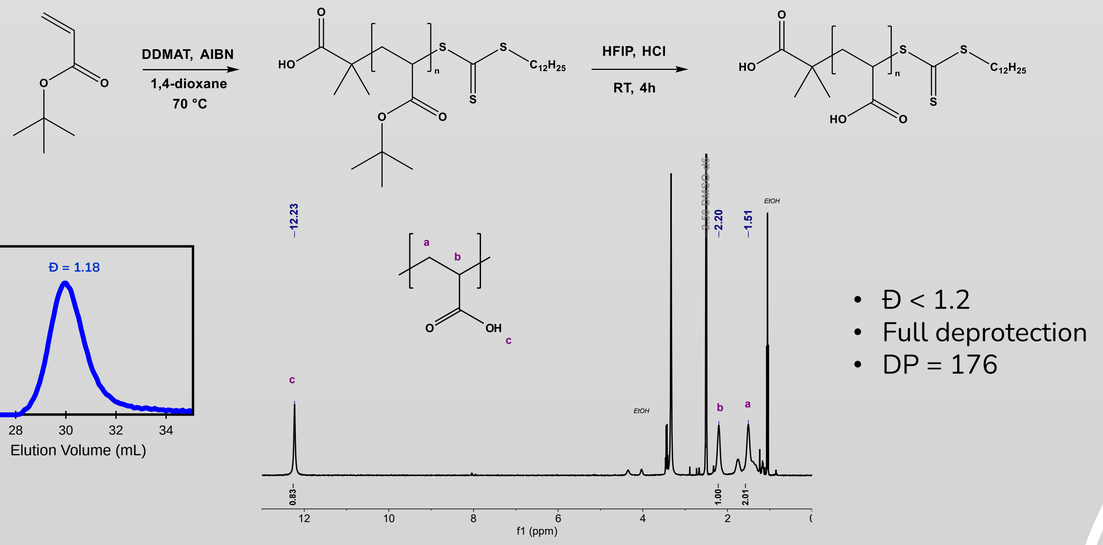




Polymer Synthesis

Polyanion Synthesis

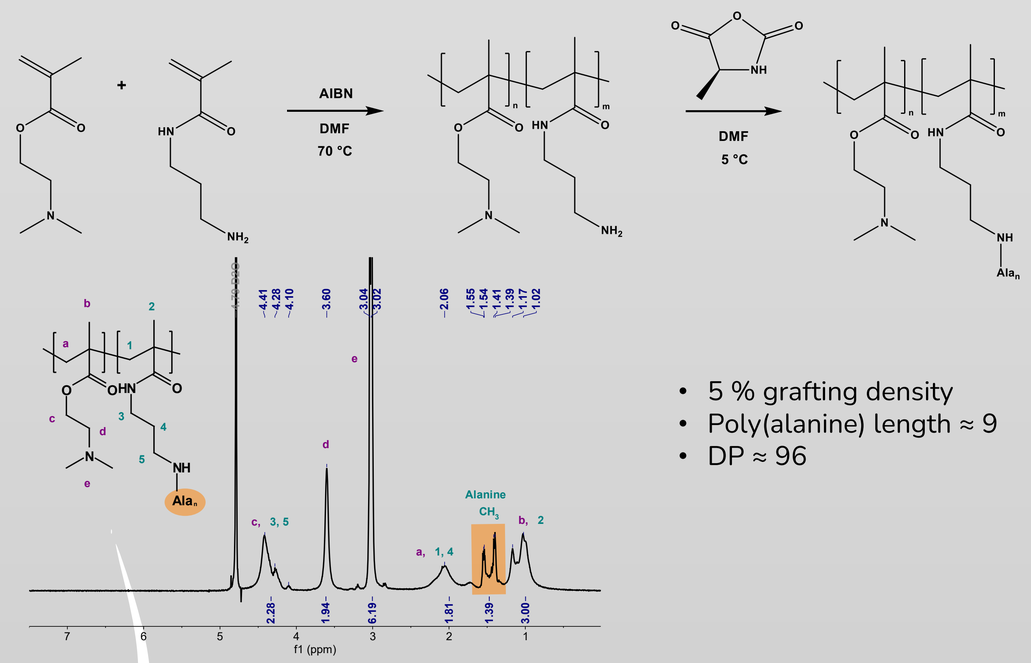
RAFT polymerization of tBA & deprotection to PAA:



- Đ < 1.2
- Full deprotection
- DP = 176

Polycation Synthesis

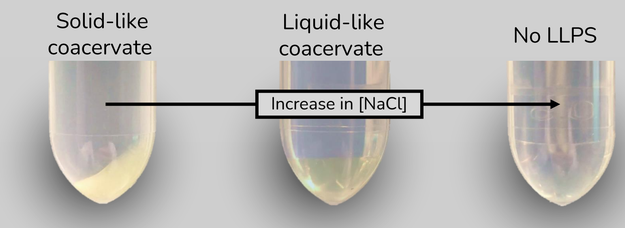
Free radical copolymerization of DMAEMA + APMA & NCA ring-opening polymerization of polyalanine:



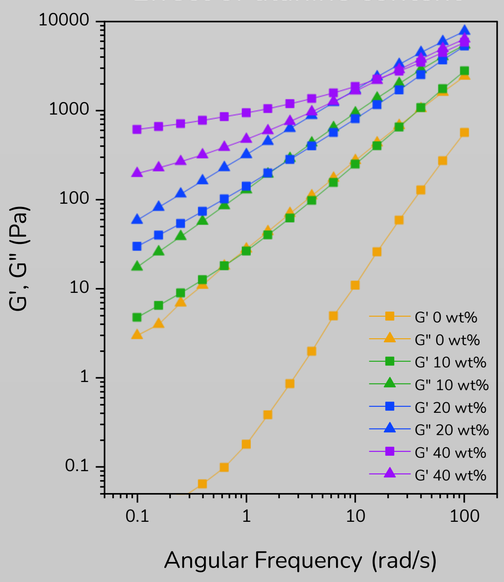
- 5 % grafting density
- Poly(alanine) length ≈ 9
- DP ≈ 96

Complex Coacervation

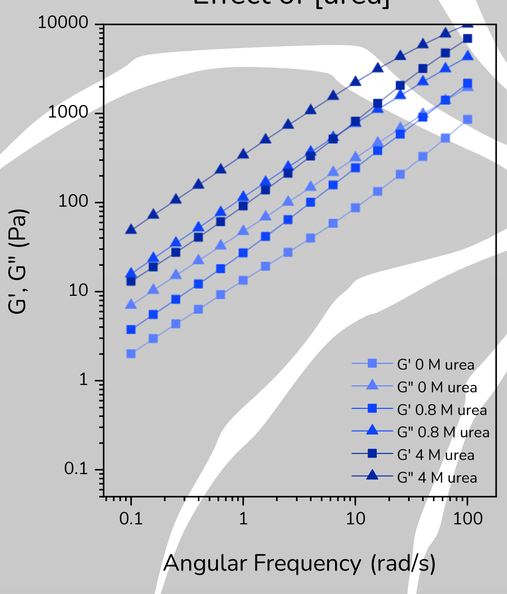
Using PAA and varied mixtures of PDMAEMA homopolymer & PDMAEMA-PAla, the complex coacervation behavior of the polyelectrolyte pair was investigated. The effect of ionic strength, alanine content, and addition of chaotropic agent urea was investigated using rheology.



Effect of alanine content

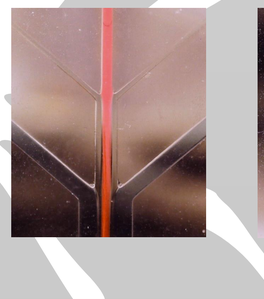


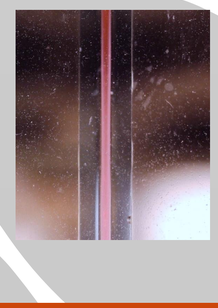
Effect of [urea]

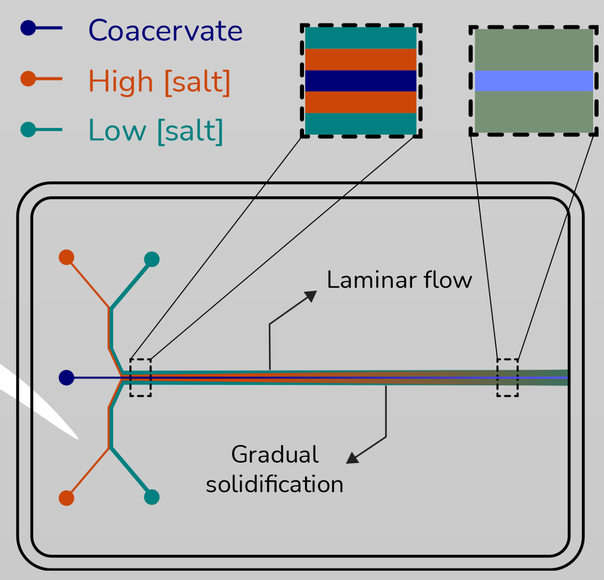


Fiber Formation

We use microfluidics to spin the liquid complex coacervate into a solid fiber. We are currently testing out various chip designs to spin complex coacervates made from commercially available polyelectrolytes poly(sodium 4-styrenesulfonate) (PSS) and poly(diallyldimethylammonium chloride) (PDADMAC) along a salt gradient.



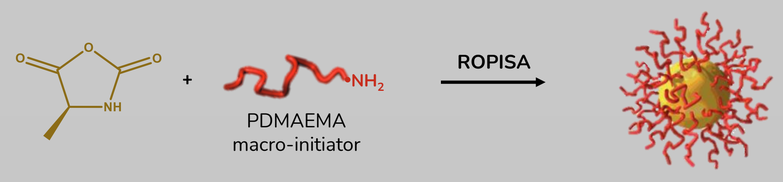




Outlook

New Polymer Architectures: Synthesize and incorporate PDMAEMA/polyalanine block copolymers via aqueous ring-opening polymerization induced self-assembly (ROPISA).

Characterization: Use *in-situ* scanning-SAXS to image α-helix to β-sheet transitions. Study the mechanical properties of the obtained fibers with DMA and tensile testing.



Proposed method for preparing PDMAEMA/poly(alanine) block copolymers via aqueous ROPISA. Image adapted from [3].

References & Acknowledgements

[1] Agnarsson, I et al. (2010). PLoS ONE 5, e11234

[2] Oktaviani, NA et al. (2018). Nat. Commun. 9, 2121

[3] Grazon, C et al. (2020). Angew. Chem. Int. Ed. 59, 622-626

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