



Precise Spacing of Pendant Vinyl Crosslinking Functionality Along a Polymer Chain

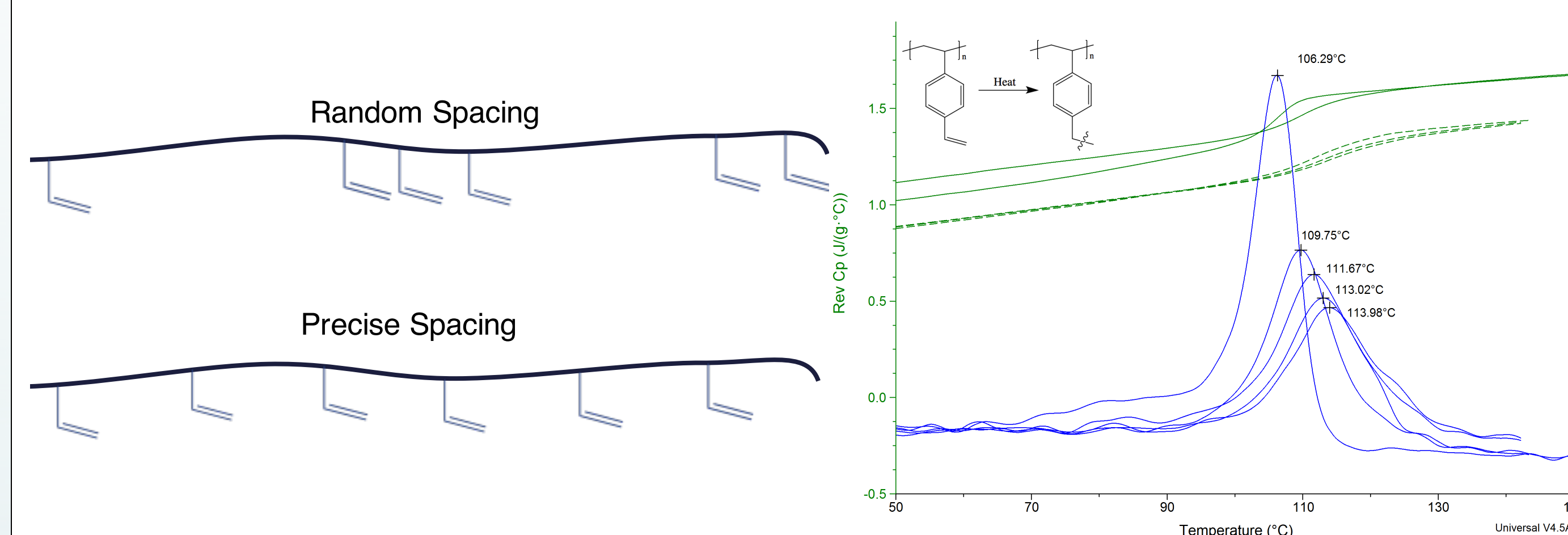
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Introduction

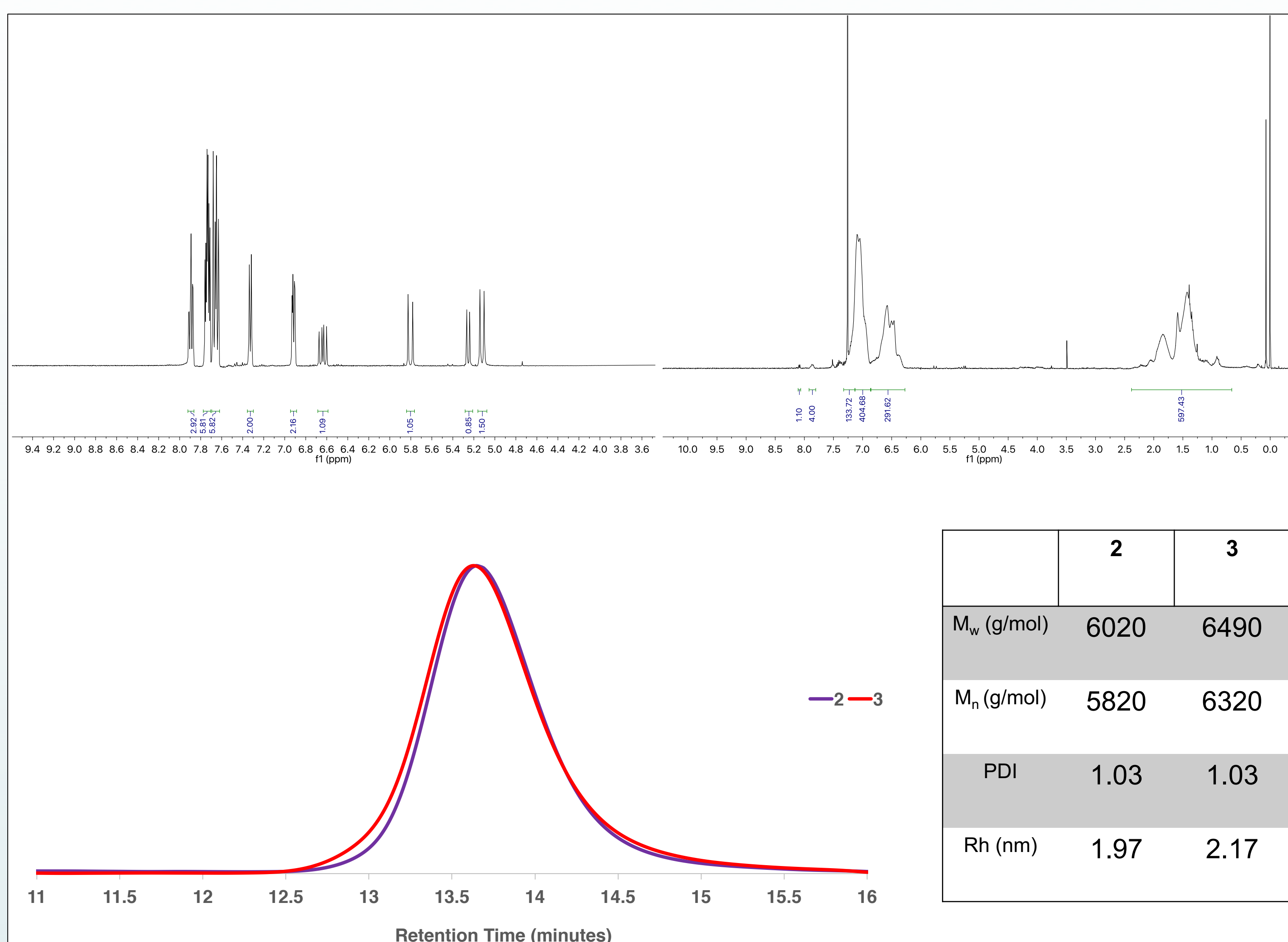
Many polymers used in industry today are crosslinked by addition of a crosslinker to the polymerization, however some are crosslinked post-polymerization. Both of these methods leads to a random (wide) distribution of crosslinking functionality along the polymer chain, and therefore a random crosslink density distribution. This study focuses on the synthesis of a polymer chain with precise spacing between pendant vinyl crosslinking functionalities. Once prepared, the polymers can then be crosslinked to form a polymer network with a more narrow crosslink density distribution. Thermal and mechanical properties of properties of the linear and networked polymer can then be compared to analogous polymers without precise spacing of crosslinking functionality.



Previous work has been done in the polymerization of protected crosslinkers (DVB, EDGMA) and post-polymerization deprotection to yield a pendant crosslinking functionality embedded in polymer chains. To maintain precise spacing between crosslinkers, a polymerization method that targeted monodisperse polymer chains was needed. Nitroxide mediated polymerization (NMP) was chosen due to its slow propagation of styrenic monomers, high molecular weight control, and low polydispersity products. NMP coupled with a protected crosslinker and comonomer, would allow for the precise spacing between crosslinking functionalities without crosslinking during polymerization.

Results and Discussion

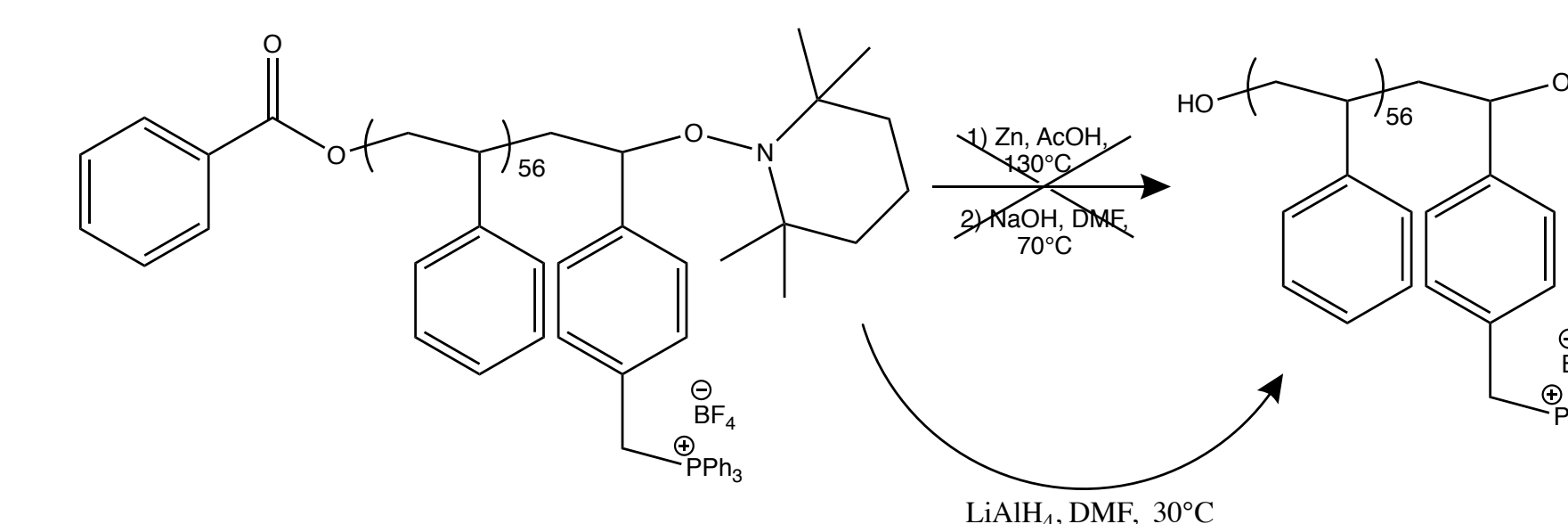
Synthesis of **1** was accomplished successfully following a procedure by Tsarevsky. Nitroxide mediated polymerization of styrene to form **2** was accomplished and characterized by NMR, DSC, and SEC.



The increase in polymer molecular weight given by SEC data showed that TEMPO-mediated chain-growth polymerization to synthesize **3** was successful with only one unit of **1** added to form the block copolymer. This is partly due to the 1:1.2 ratio of **2** and **1** respectively added to the reaction and the slow kinetics of TEMPO-mediated (NMP) styrenic polymerization.

Work in Progress

The lack of polymer solubility, and choice of weak reducing agent to reduce the alkoxyamine and ester both led to the unsuccessful synthesis of diol **4**. The polymer demonstrated low solubility at moderate temperatures in acetic acid and with the low solubility zinc dust, the alkoxyamine could not be reduced similar to literature. Stronger reducing agents like LiAlH₄ and NaBF₄ might prove successful, however might deprotonate the protection group to form a triphenylphosphine ylide.



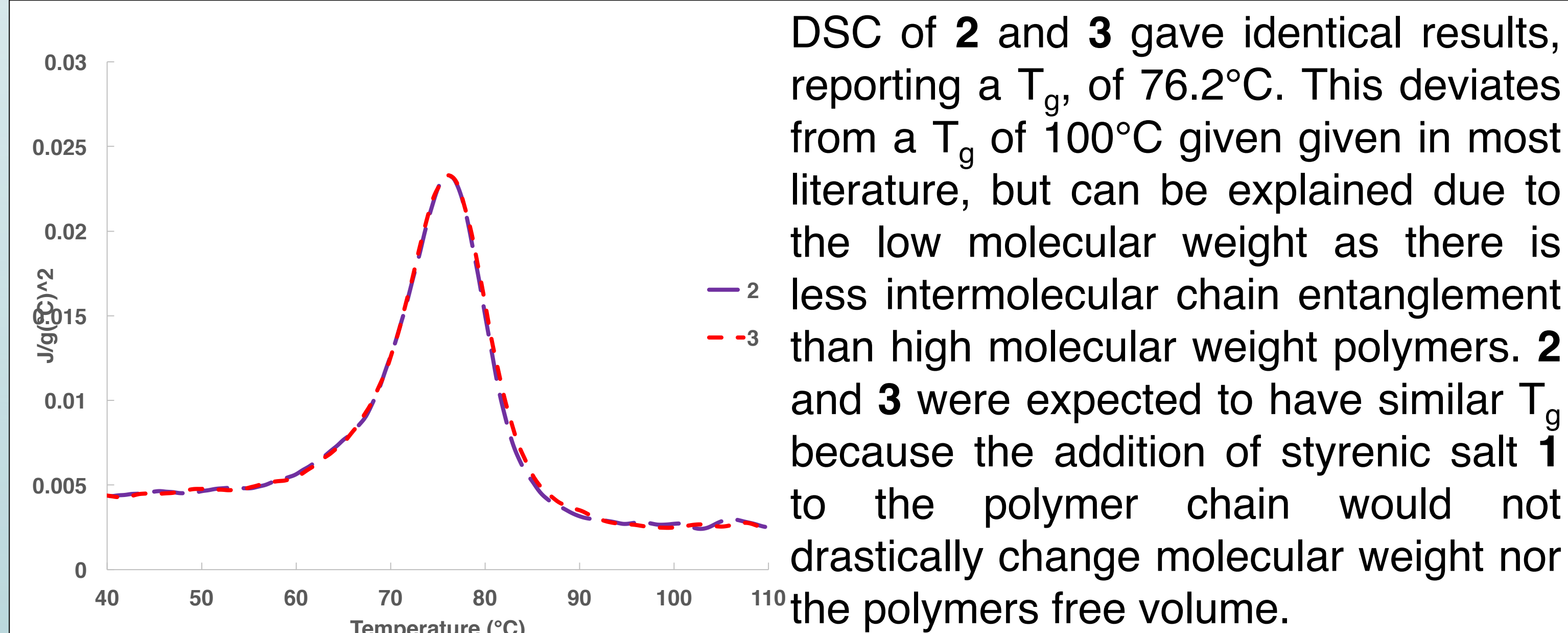
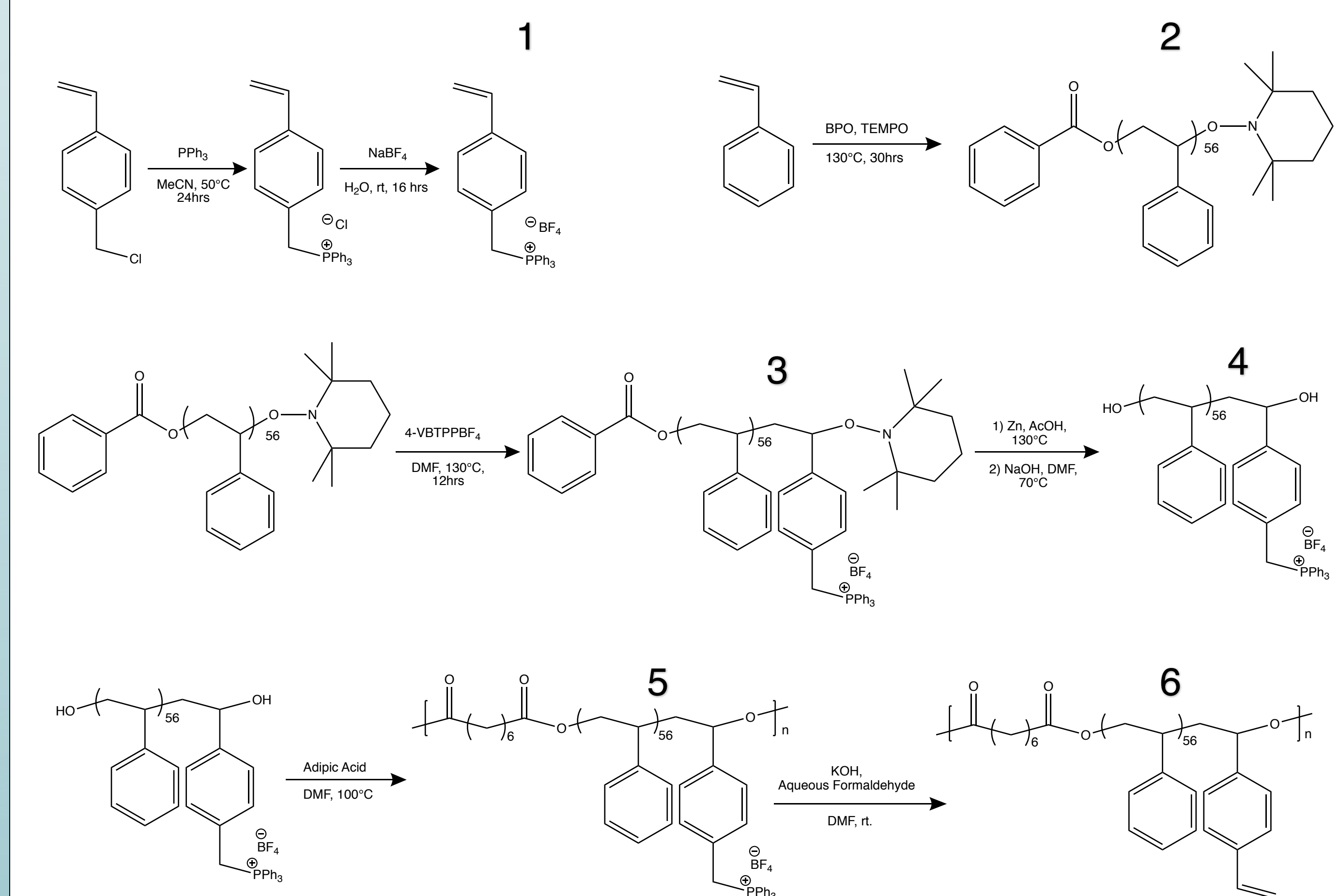
Summary and Future Work

The synthesis and characterization of **1,2**, and **3** was successful. However, the synthesis of **4** was incomplete as conditions and choice of reducing agent for the reduction of the ester and alkoxyamine to a diol proved challenging. The synthesis and characterization of **1,2**, and **3** was successful. Better reducing agents (LiAlH₄, NaBF₄, SnI₂, etc..) might prove more successful in synthesizing **4**.

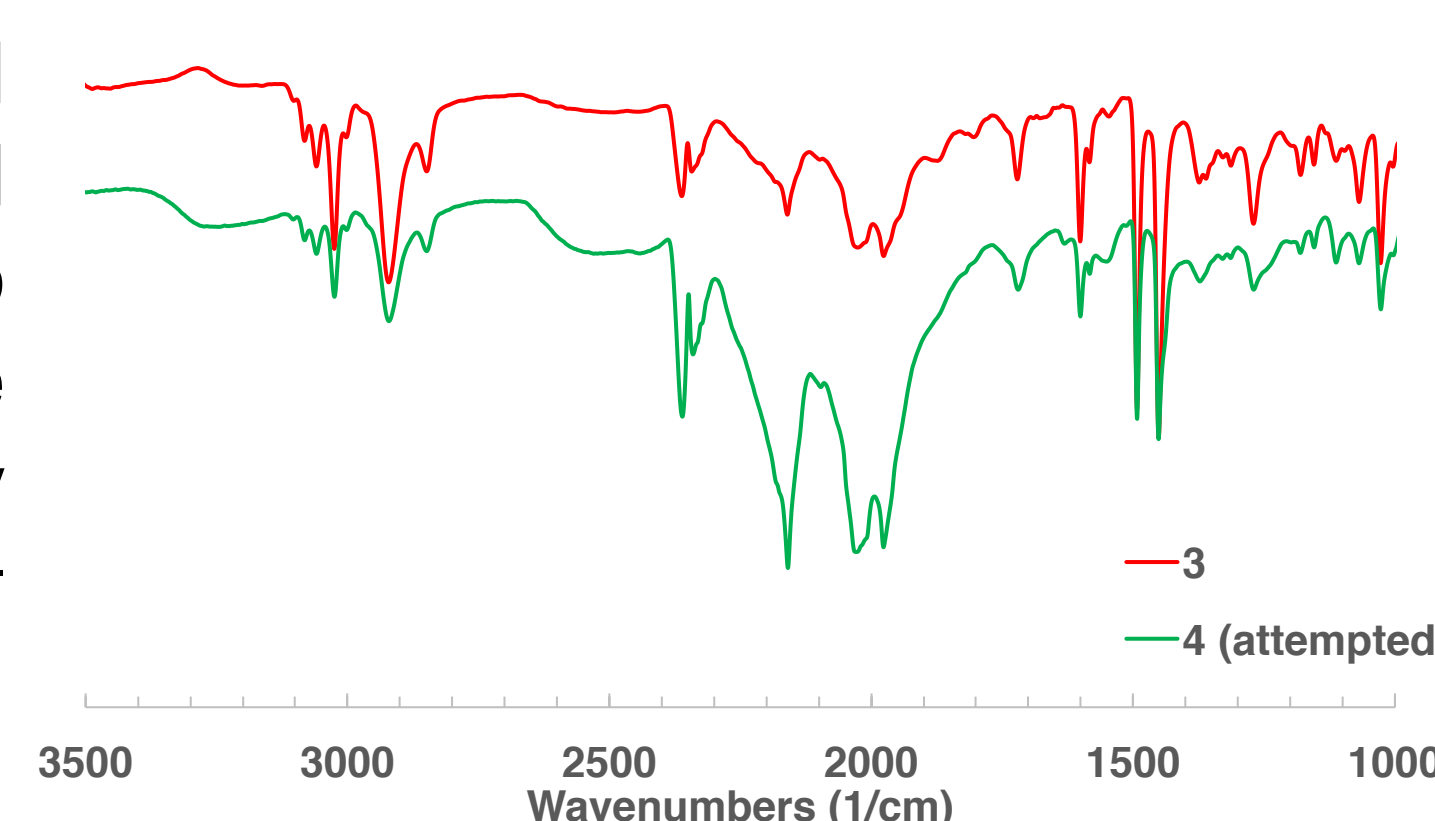
Once **4** has been synthesized, the step growth condensation polymerization with adipic acid to form polyester **5** will be attempted. Finally, a Wittig olefination will be conducted to form **6**, a pendant vinyl crosslinking functionality with precise spacing along a polymer chain.

The thermal and mechanical properties of **6** can then be tested and compared to polymers with random incorporation of crosslinking functionality.

Synthetic Scheme



The reduction of the alkoxyamine and ester of **3** to form diol **4** was attempted and proved unsuccessful. This is due to weak reducing agent initially used. The reactant and products showed nearly identical FTIR spectra; ester at 1730cm⁻¹, and TEMPO at 1500 and 1450cm⁻¹.



Acknowledgements

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References

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