

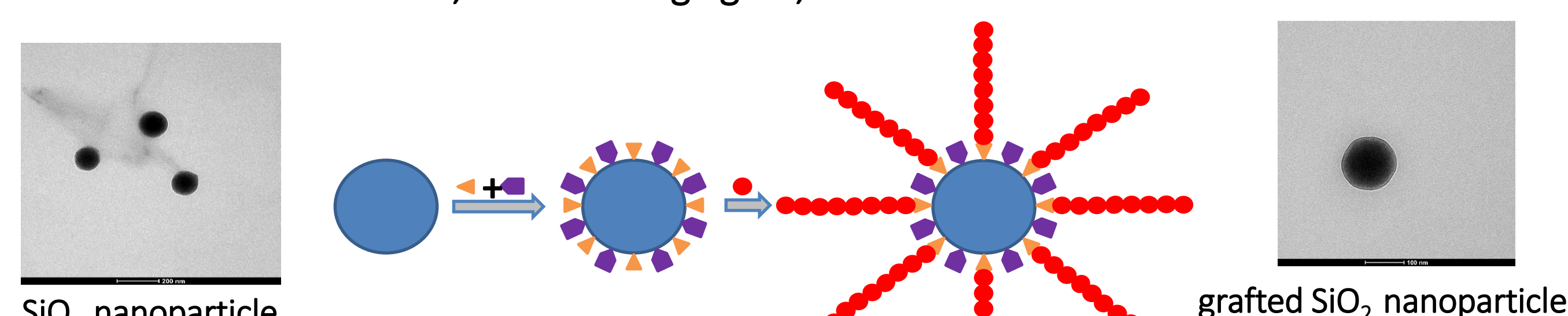
Introduction

Abstract

Ejaz et al (2015) demonstrated the potential for silica nanoparticle-based oil dispersants. In contrast to traditional dispersants, such dispersants maintain emulsion and structural integrity at much greater dilution.² Through control of grafting density and length of the polymer chains grafted to the nanoparticle surface, the pore size is altered, potentially affecting its encapsulation ability.

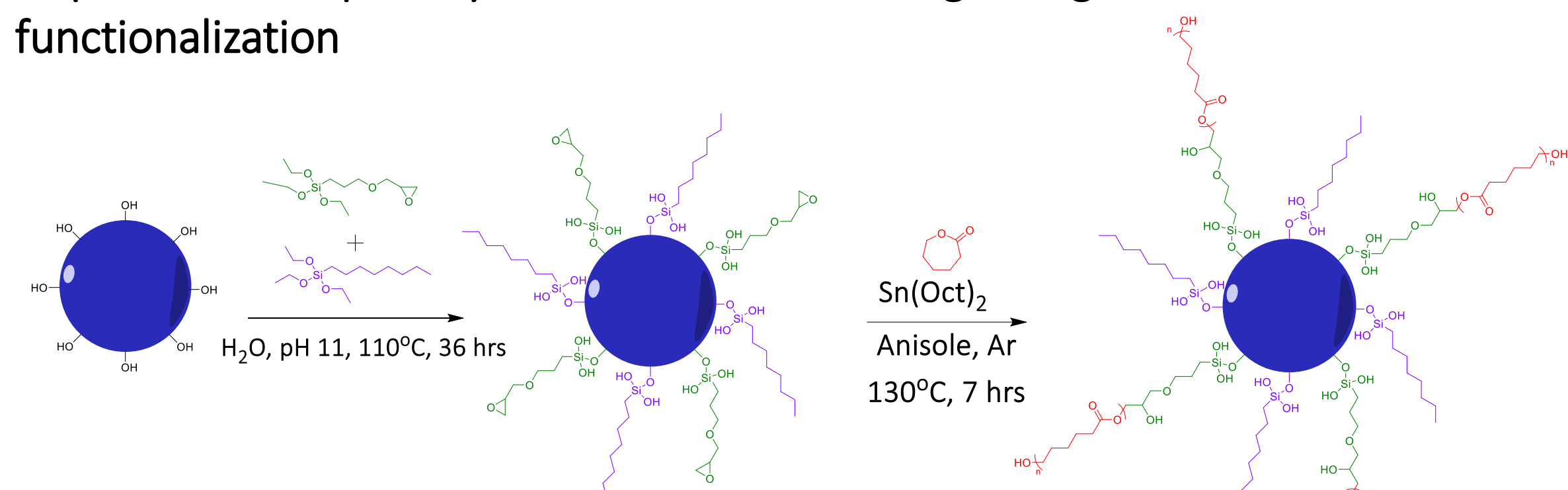
Overall Goals

- To control the grafting density of ϵ -caprolactone polymer chains grafted from SiO_2 -GPS through surface-initiated ring opening polymerization (SIROP).
- To determine variation in grafting density produced by functionalizing nanoparticles with fractions of unreactive OTS, as a blocking agent, in addition to GPS.



Specific Aims

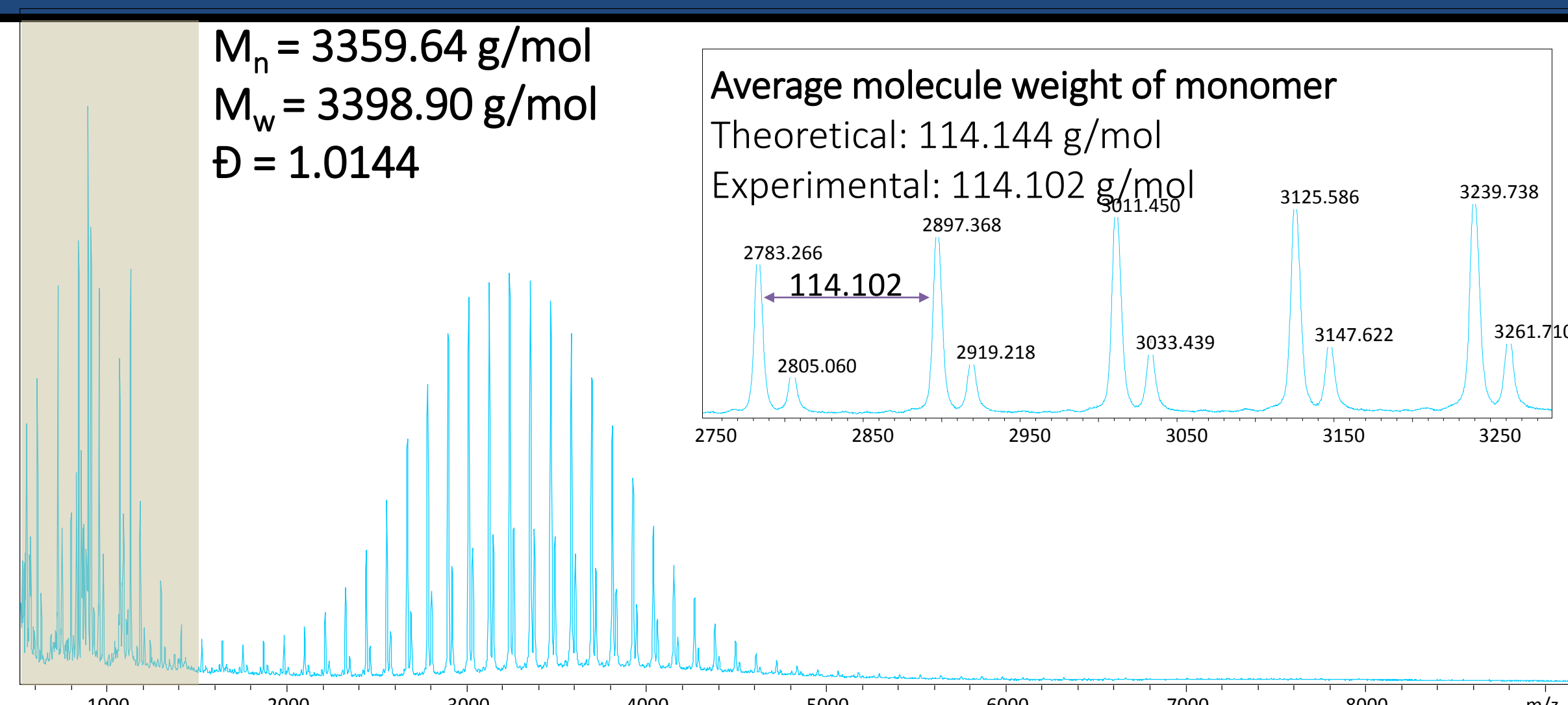
- Determination of the mass of grafted poly(caprolactone) by comparison with in-situ poly(caprolactone)
- Calculation of grafting density through mass loss of attached poly(caprolactone)
- To achieve high molecular weight poly(caprolactone) with a low dispersity
- To produce and quantify variation in number of grafting sites due to OTS functionalization



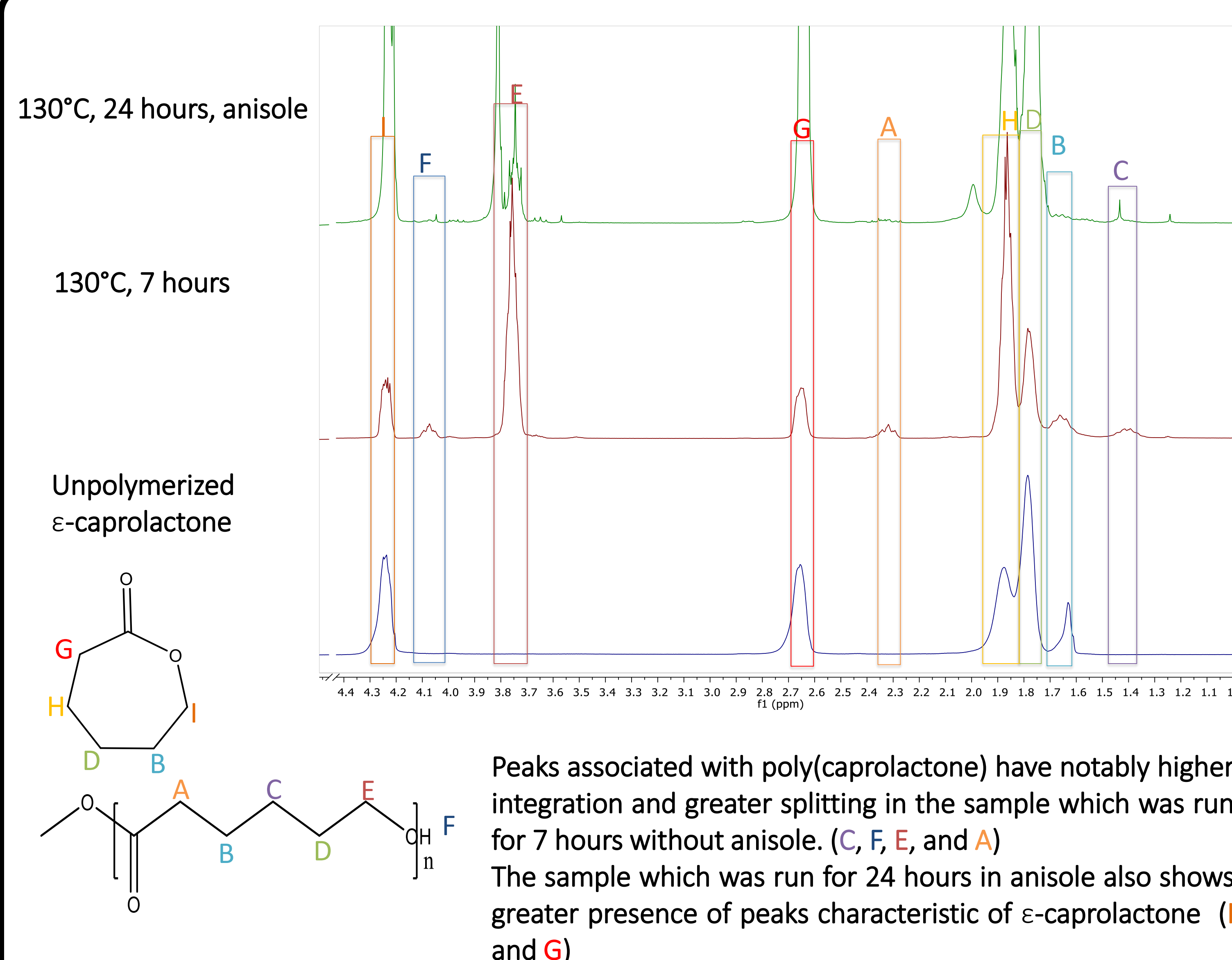
Background

Following the work of Dr. Muhammad Ejaz, Silica nanoparticles (SiO_2) are functionalized with 3-glycidyloxypropyltriethoxysilane (GPS). Then via surface-initiated ring opening polymerization (SIROP) of ϵ -caprolactone, poly(caprolactone) (PCL) chains are grafted- from the functionalized nanoparticles. A polar block may be added which allows the grafted particles to act as amphiphilic micelles, as shown by Ejaz et al.² The amphiphilicity of the particles is controlled, in part, by the length of the PCL chain which forms the nonpolar region. The pore size of the nanoparticle's corona would be dependent on the density of caprolactone grafting sites on its surface. Through comparison of particles functionalized with some ratio of GPS and OTS, and those with only GPS, information is gained regarding the portion of available sites as well as the degree of control which can be established through this mechanism

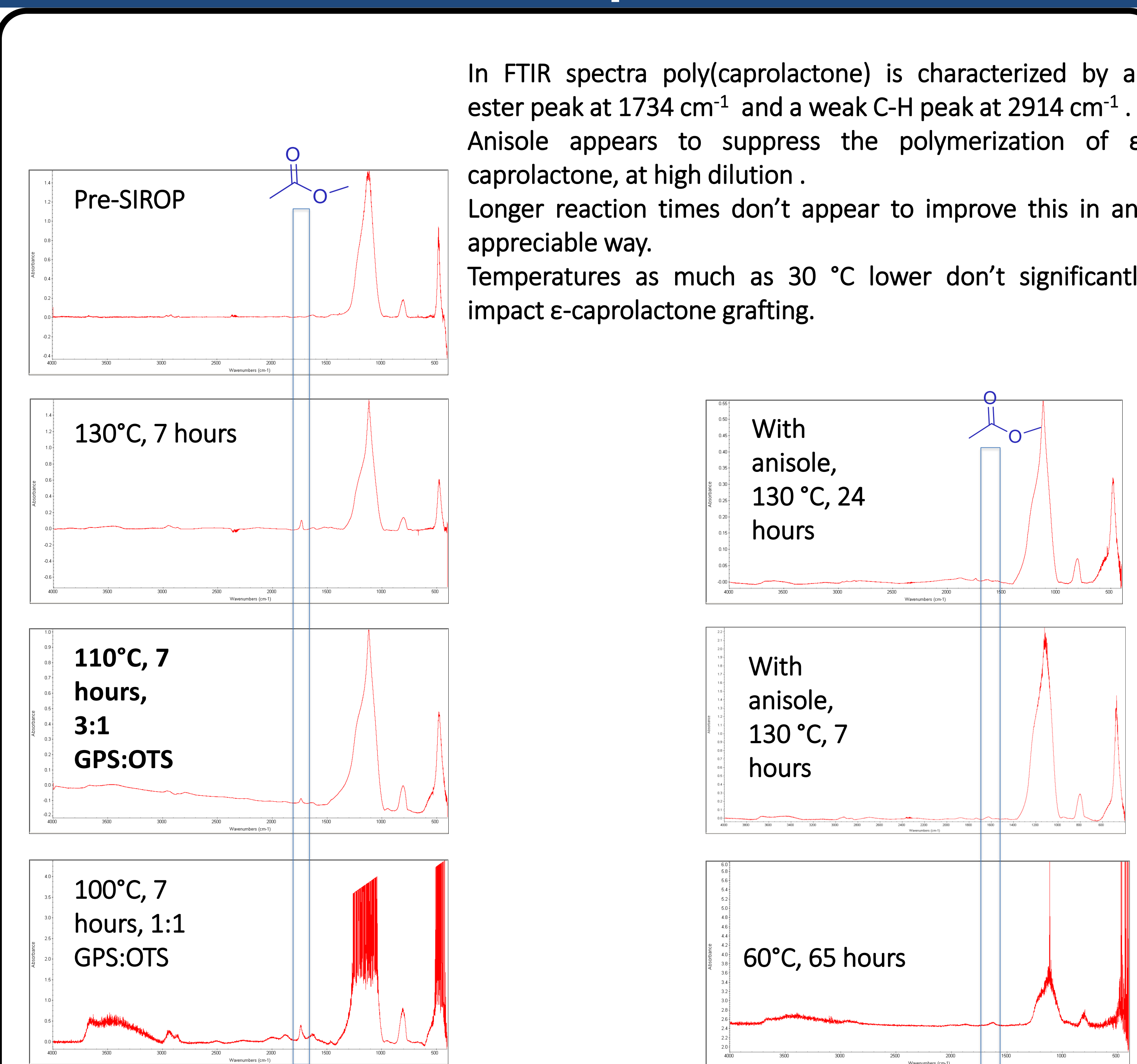
MALDI-TOF of free PCL



NMR of Free PCL

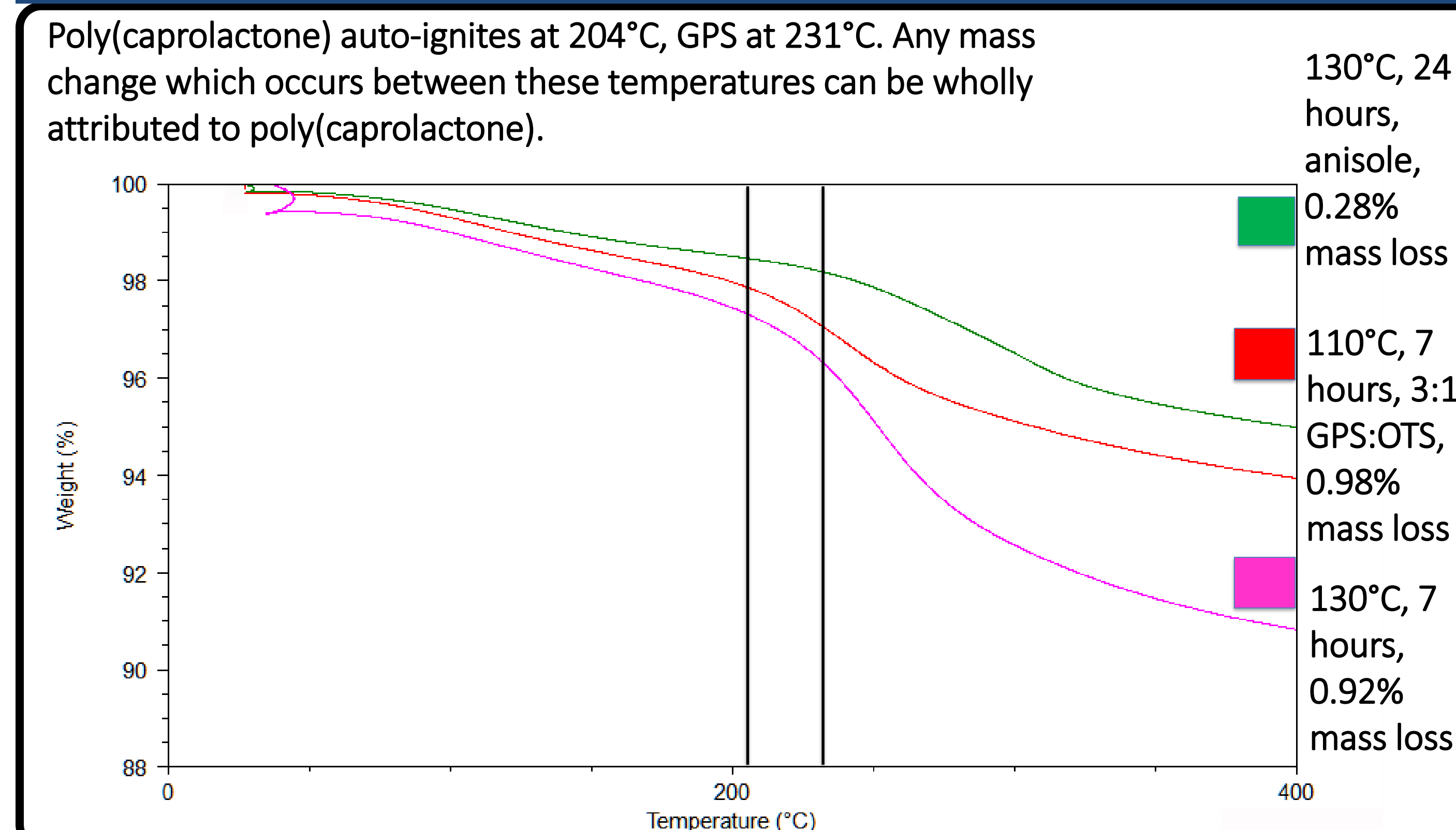


FTIR Comparison



In FTIR spectra poly(caprolactone) is characterized by an ester peak at 1734 cm^{-1} and a weak C-H peak at 2914 cm^{-1} . Anisole appears to suppress the polymerization of ϵ -caprolactone, at high dilution. Longer reaction times don't appear to improve this in any appreciable way. Temperatures as much as 30°C lower don't significantly impact ϵ -caprolactone grafting.

TGA of grafted particles

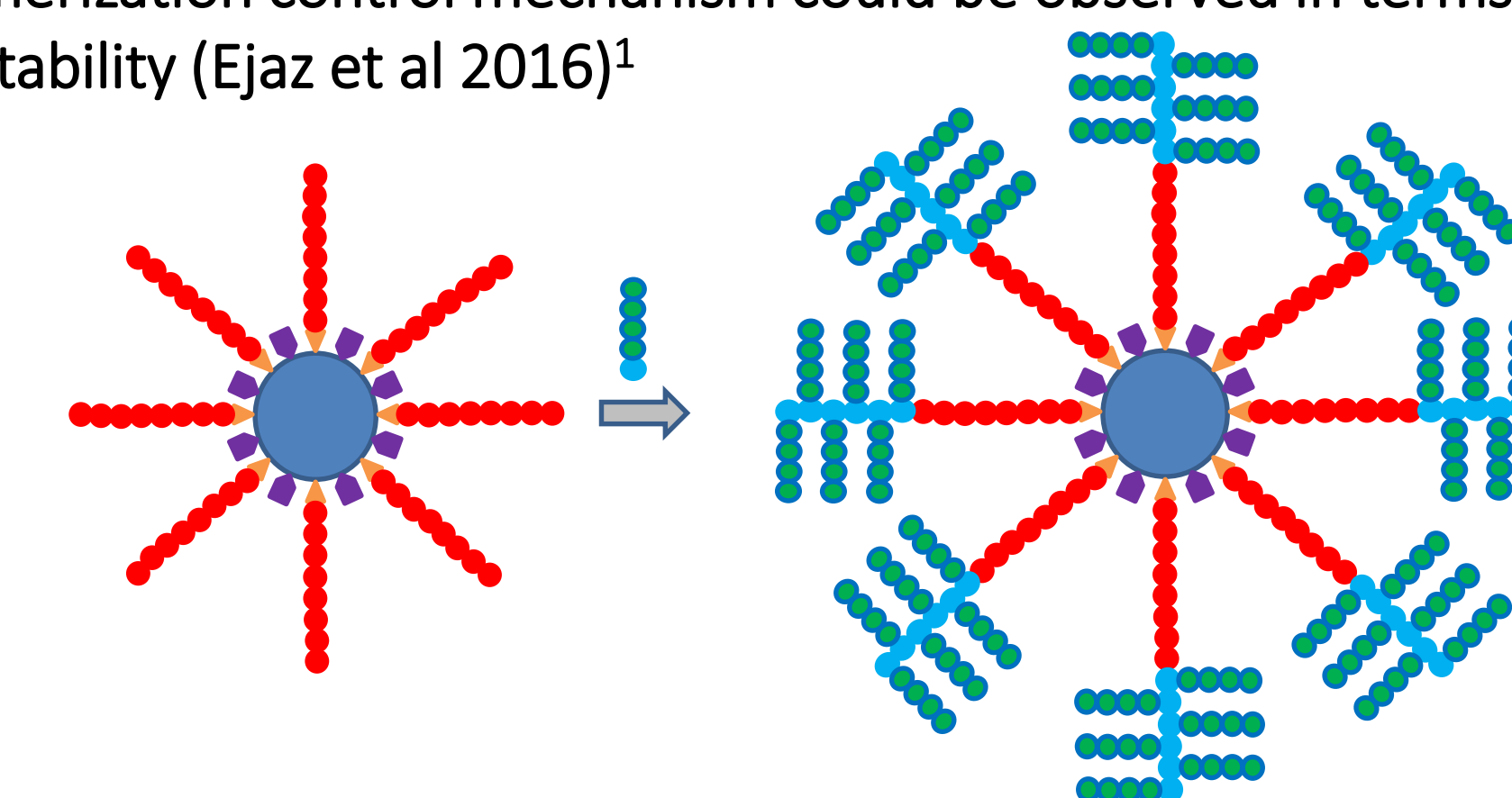


Conclusions

- Anisole, in the volume used, impedes ϵ -caprolactone polymerization
- Poly(caprolactone) can be grafted at temperatures as low as 60°C , given an adequately long time frame
- The GPS:OTS ratios used do not allow control over grafting density, suggesting that relatively few of the available grafting sites are used

Further Research

- Sonication at various intensities should be applied to the grafted nanoparticles, so that a threshold for their degradation may be established
- Proportionally greater amounts of OTS could be used successively to more exactly estimate the number of grafting sites
- Solvents could be tested as a control mechanism
- Hyperbranched poly(ethylene glycol) could be added as a polar block so that the effects of any polymerization control mechanism could be observed in terms of encapsulation ability and stability (Ejaz et al 2016)¹



References

- Muhammad Ejaz, A. M. A., Scott M. Grayson, Amphiphilic hyperbranched polyglycerol-block-polycaprolactone copolymer-grafted nanoparticles with improved encapsulation properties. *Reactive and Functional Polymers* 2016, 102, 39-46.
- Muhammad Ejaz, A. M. A., Karolina A. Kosakowska, and Scott M. Grayson, Modular amphiphilic copolymer-grafted nanoparticles: "nanoparticle micelle" behavior utility as dispersants. *Polymer Chemistry* 2015, 6, 7749-7757.

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