



# Synthesis and Characterization of Polysilsesquioxane Hybrid Melting Gels

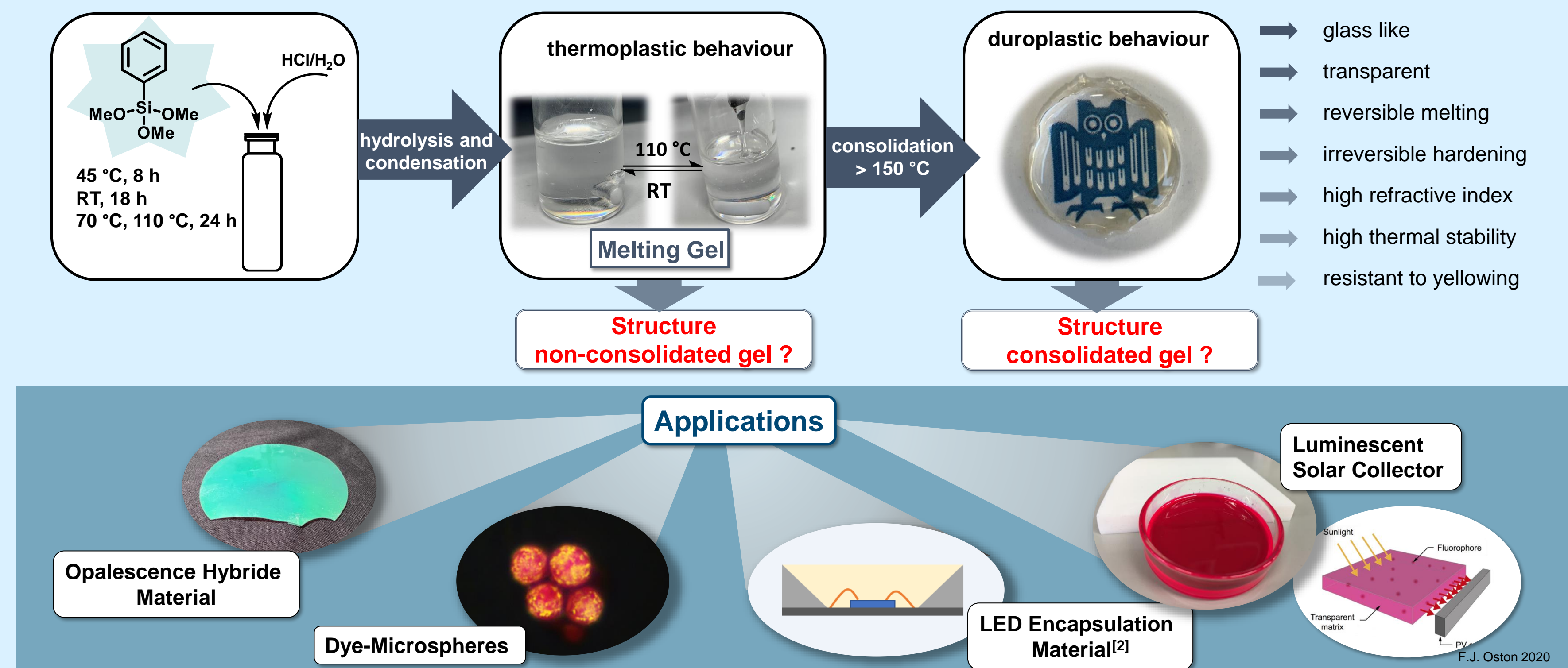
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## Introduction

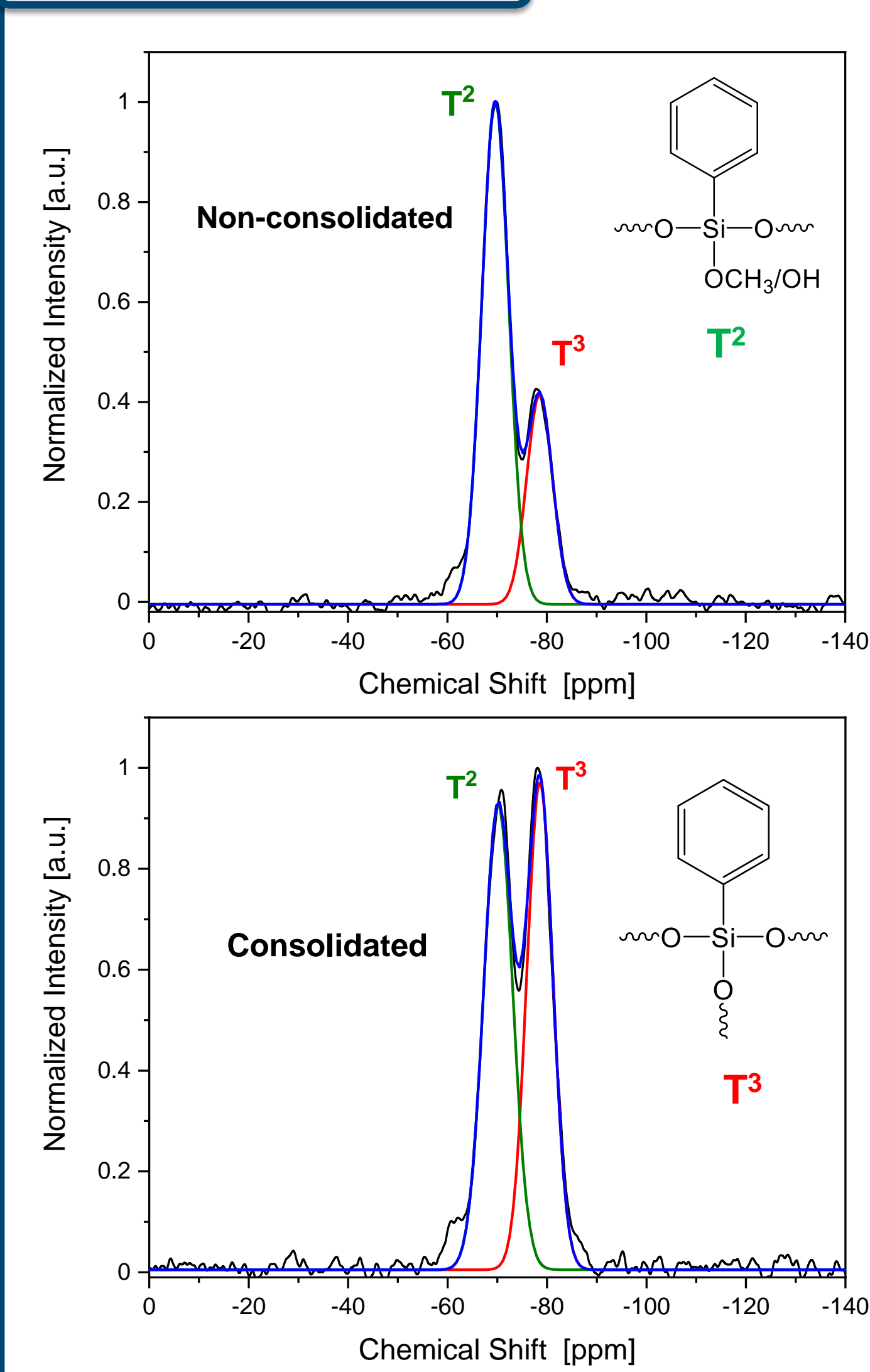
**Melting gels** are inorganic-organic compounds with siloxane and silsesquioxane units produced by a combined hydrolysis and condensation reaction of di- and trialkoxysilanes.<sup>[1,2]</sup> They are rigid, transparent materials at room temperature and soften reversibly around 110 °C. Exposure to a consolidation temperature above 150 °C results in irreversible curing to a glassy, transparent, insoluble, and thermoset material. By changing the organic groups and the ratio of di- and trialkoxysilanes, properties like refractive index, hardness, or viscosity can be varied. The platinum free curing, mild and low toxic synthesis conditions, and the wide range of adjustable properties make the material interesting for many applications also in a green chemistry context. We investigated the underlying mechanism of acid-catalyzed melting gel formation and the final structure by various spectroscopic techniques, X-ray diffraction, and thermal analysis using a polyphenylsilsesquioxane as a model system.<sup>[3]</sup> As proof of concept we studied the influence of organotrimethoxysilanes with larger aromatic groups as well as phenyltrihydroxysilanes on the melting gel properties.

## Synthesis and Applications



## Characterization and Results

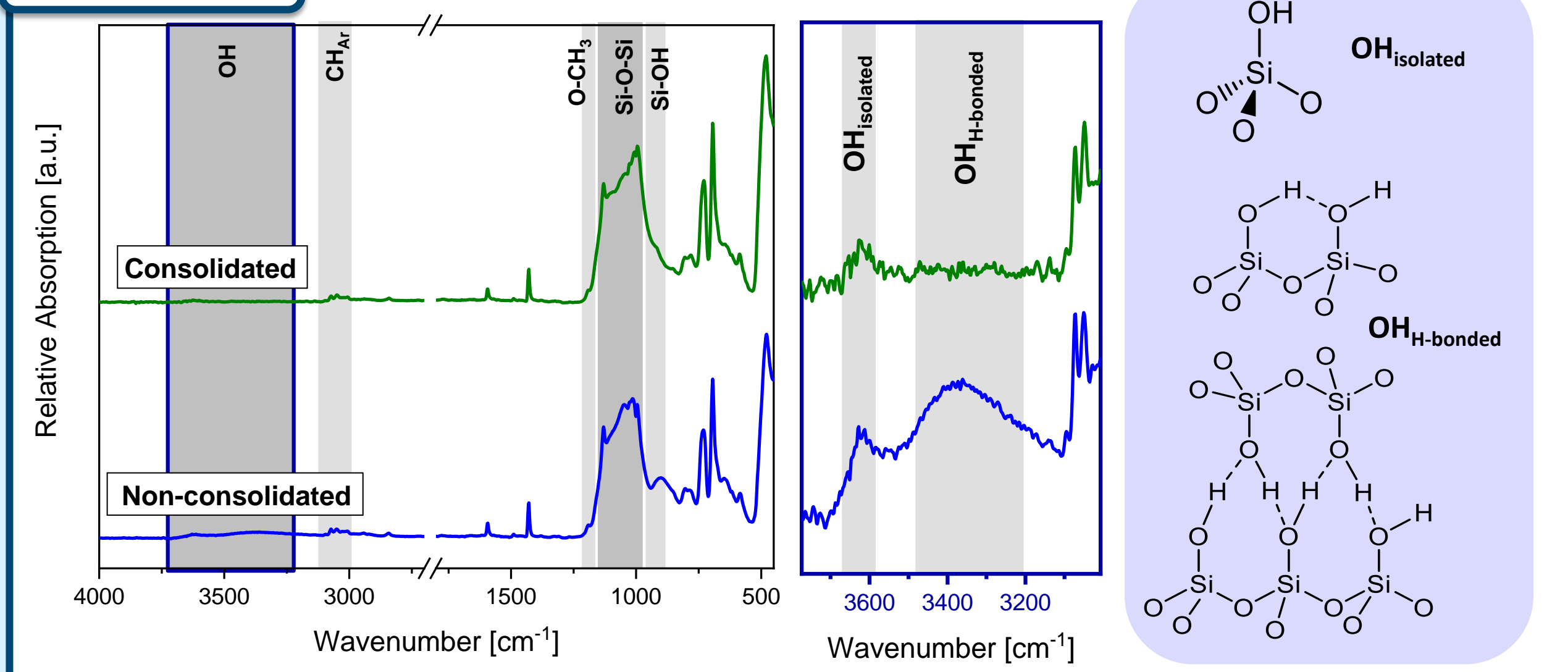
### <sup>29</sup>Si CP-MAS NMR



→ Complete integration of the PhSi(OMe)<sub>3</sub>  
→ Still non-condensed OMe- and OH-groups (OMe-Groups visible in <sup>13</sup>C CP-MAS-NMR)  
→ Higher cross-linking due to thermal curing

→ Intramolecular excimer fluorescence<sup>[4]</sup> (I<sub>M</sub>/I<sub>E</sub> = const.)  
→ π-π-interactions

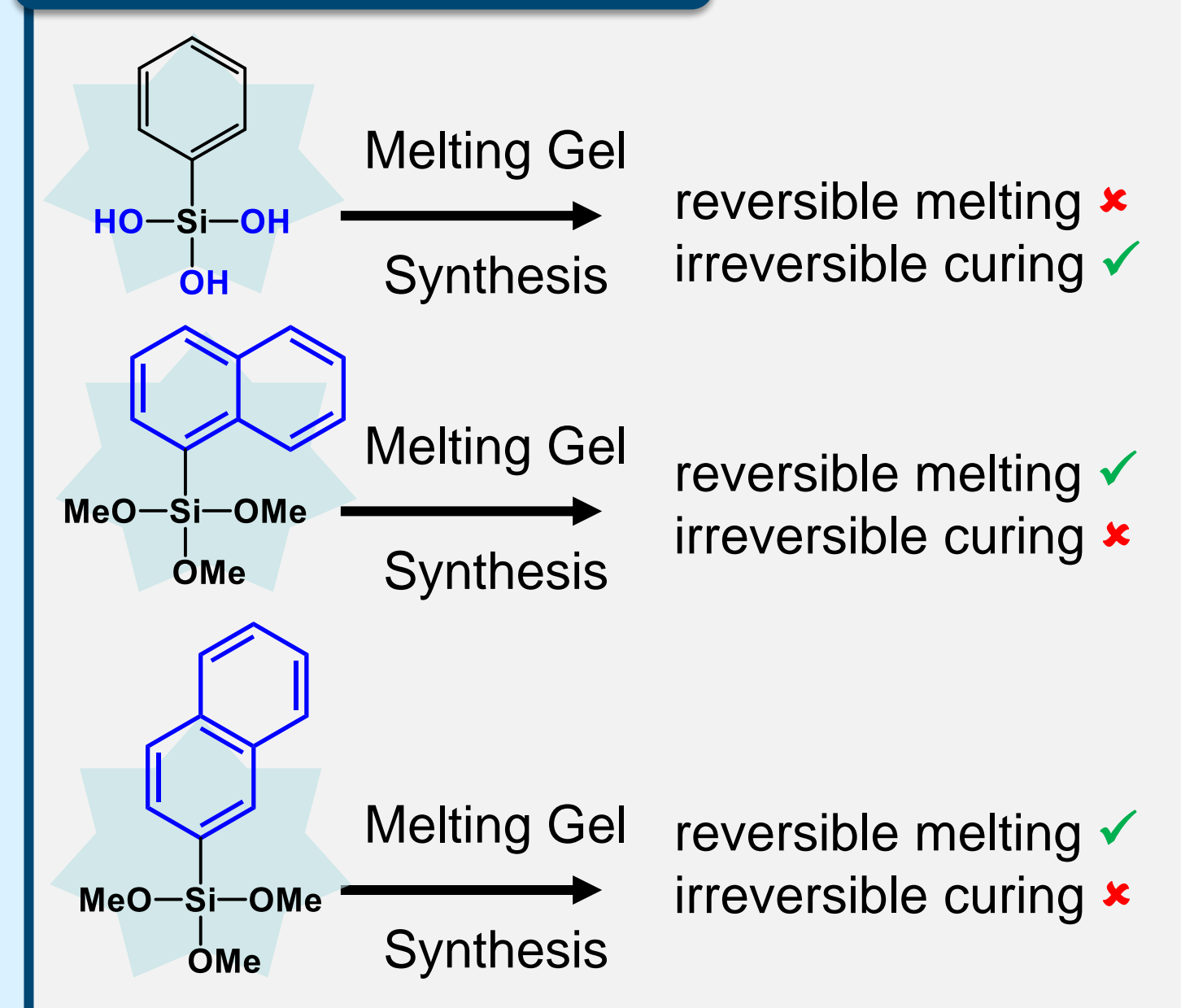
### FTIR



→ H-bonded and isolated OH-groups<sup>[6]</sup>  
→ Broad complex Si-O-Si band (1050-1000 cm<sup>-1</sup>)<sup>[7]</sup>  
= Different silsesquioxane species

→ Structure with ladder-like domains<sup>[5]</sup>  
→ Increased after consolidation (higher ratio I<sub>d1</sub>/I<sub>d2</sub>) by a reorientation of the siloxane chains and an inter- and intramolecular condensation of -OMe and -OH groups

### Further Monomers

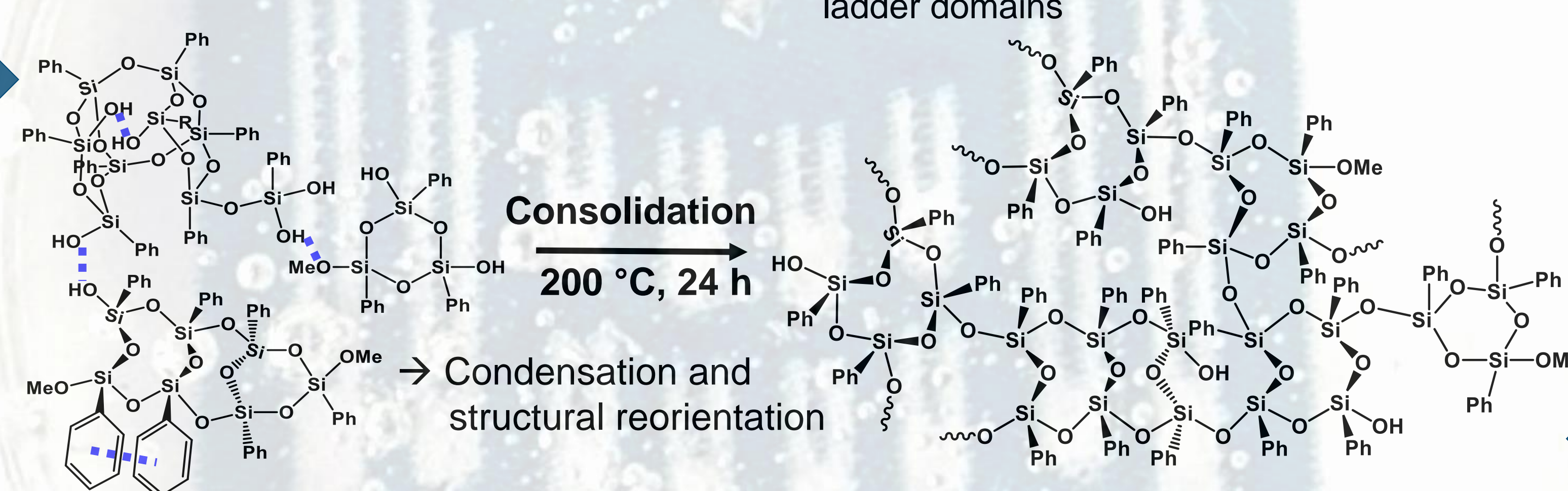


High reactivity of silanols leads to high cross-linking  
→ No reversible softening  
→ OMe-Groups required for softening

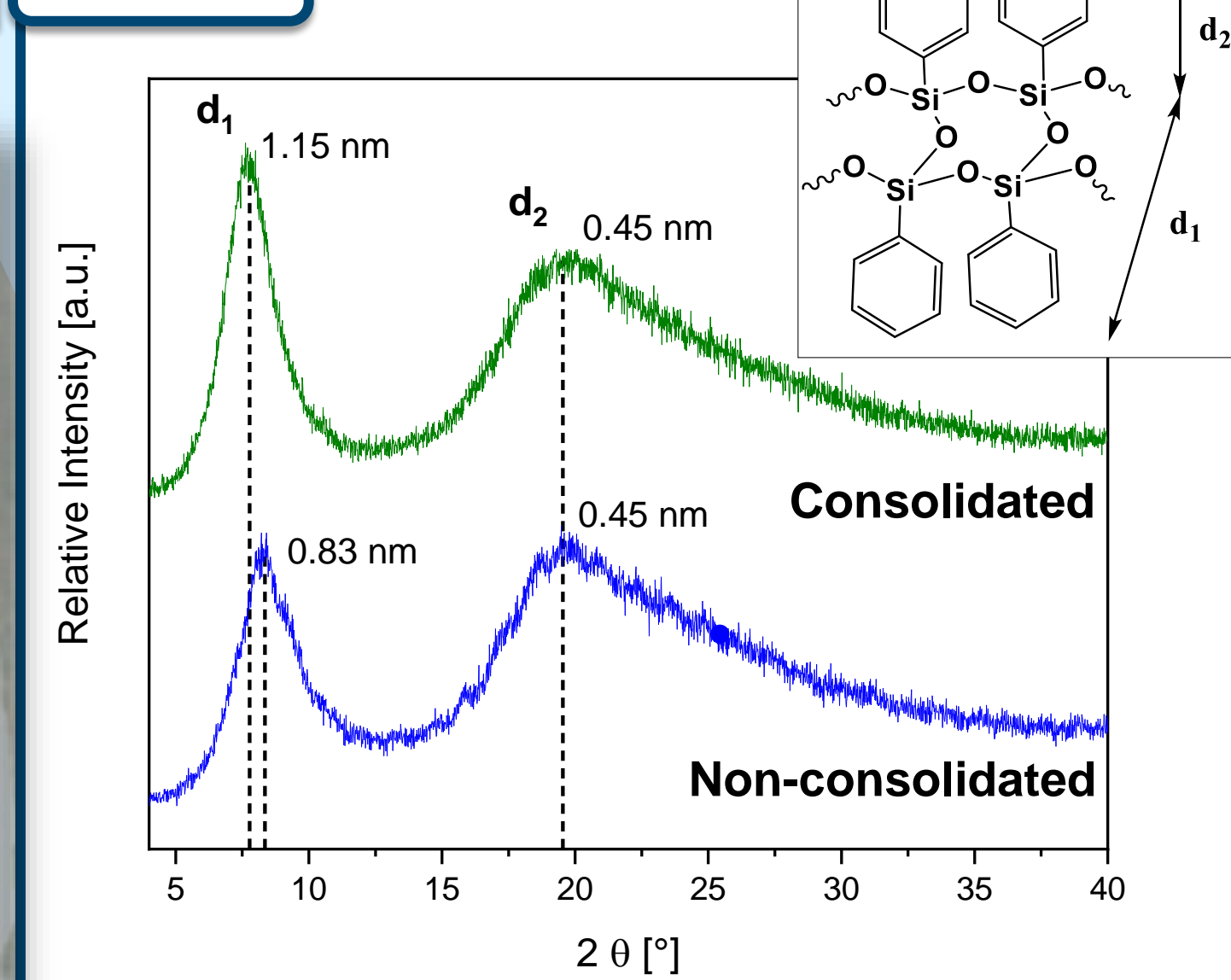
No irreversible curing after consolidation at 200 °C for 24 h due to larger steric hindrance and lower cross-linking  
→ Still softenable

Partial cross-linked defect rich network stabilized by hydrogen bonds and π-π-interactions with ladder-like domains

Highly cross-linked structure with ladder domains

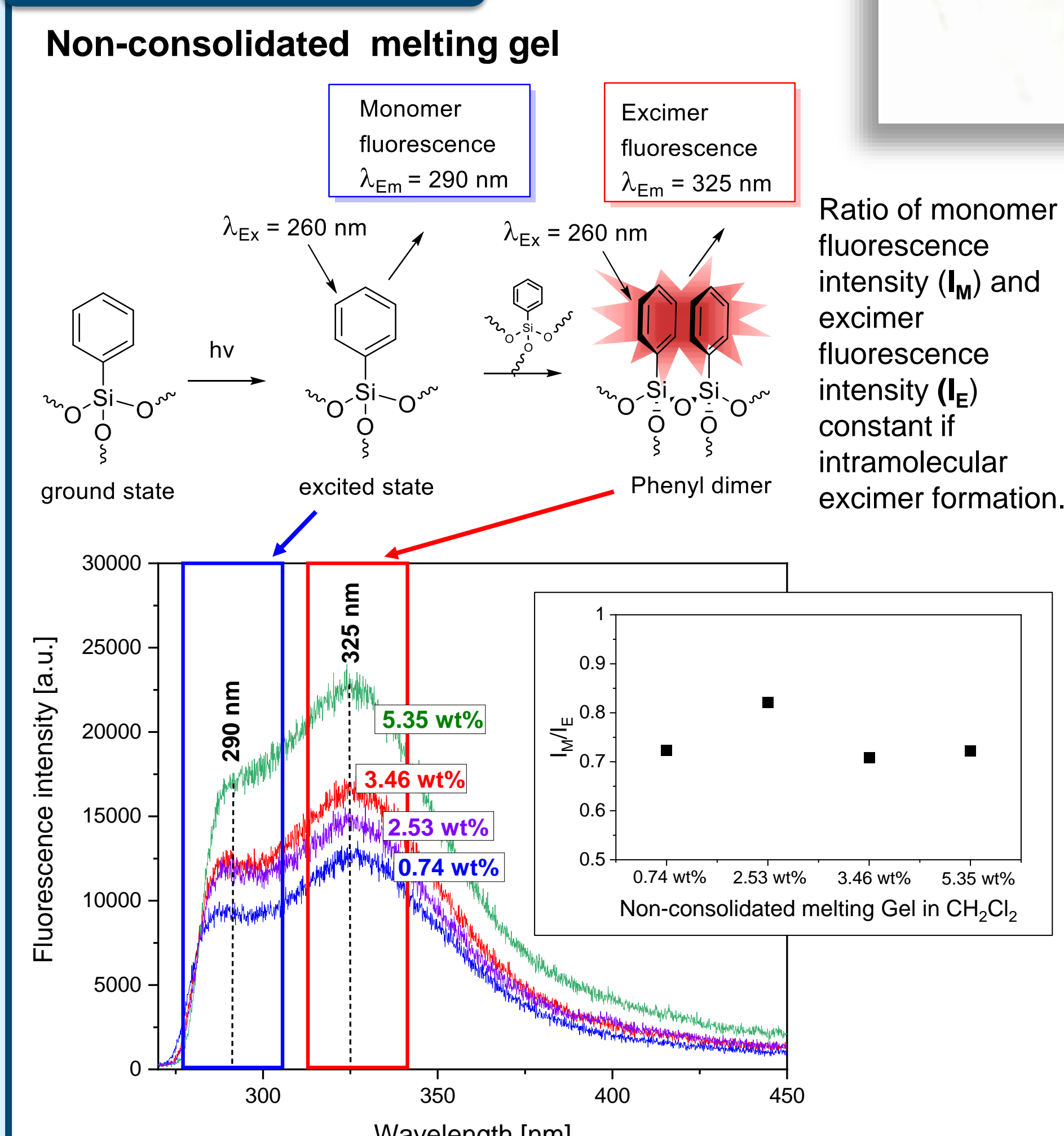


### XRD



→ No visible T<sub>g</sub> after consolidation = Irreversible curing  
→ No change of T<sub>g</sub> after three heating cycles at 110 °C = Reversible softening

### Fluorescence

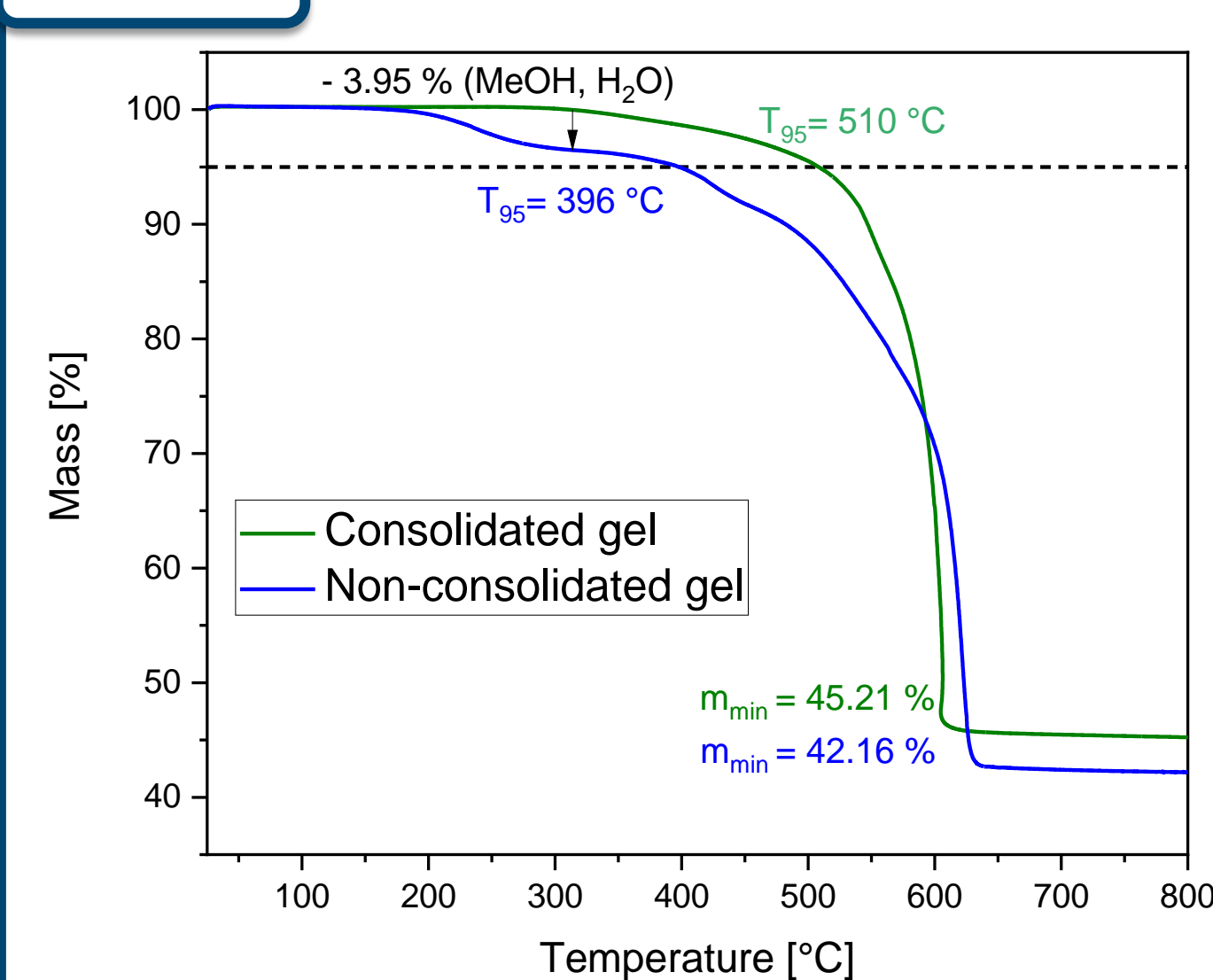


Ratio of monomer fluorescence intensity (I<sub>M</sub>) and excimer fluorescence intensity (I<sub>E</sub>) constant if intramolecular excimer formation.

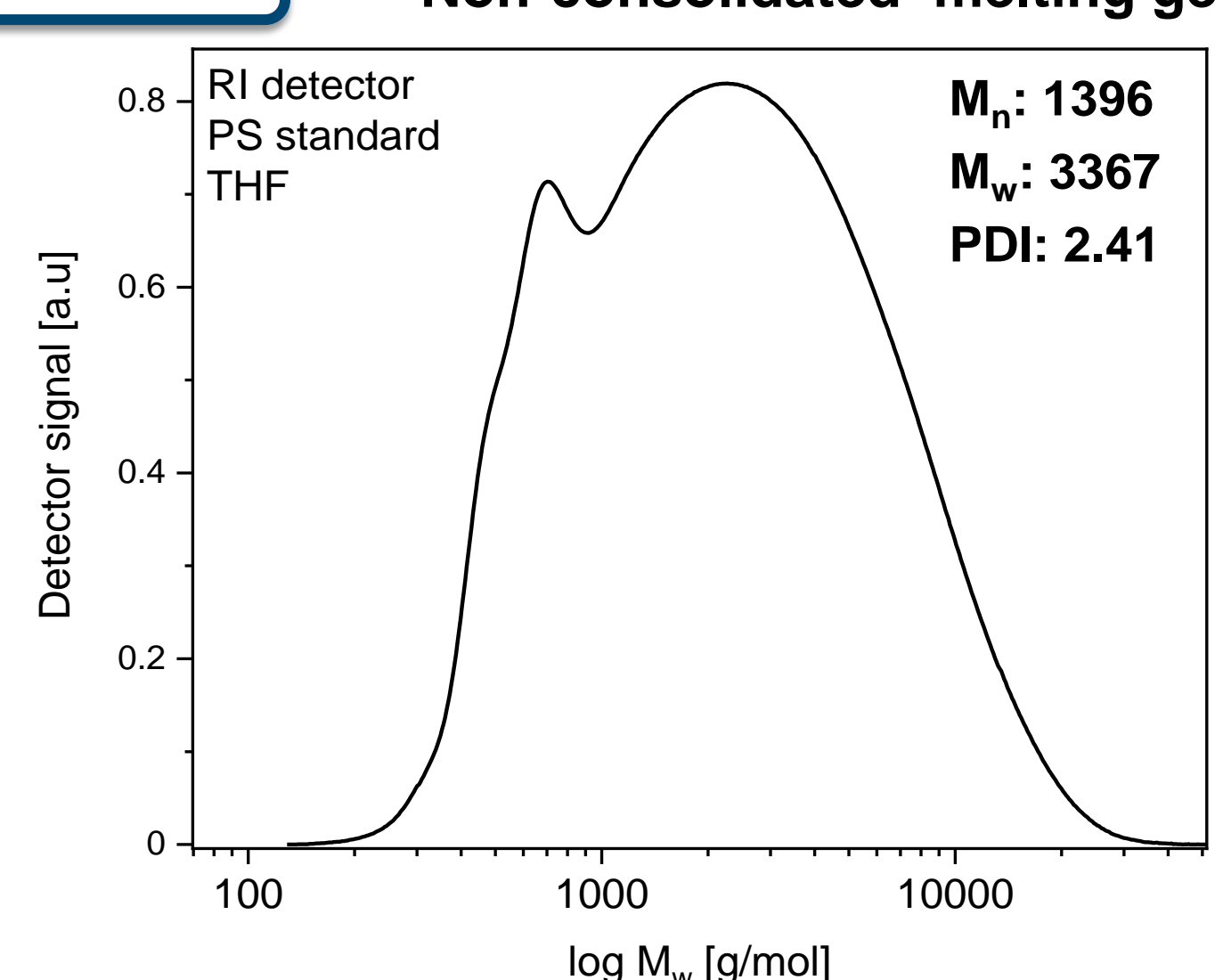
→ Low molecular weight  
→ n ≈ 6-15

→ Consolidation = Further Condensation reactions  
→ High thermal stability (T<sub>95</sub> ≈ 500 °C)

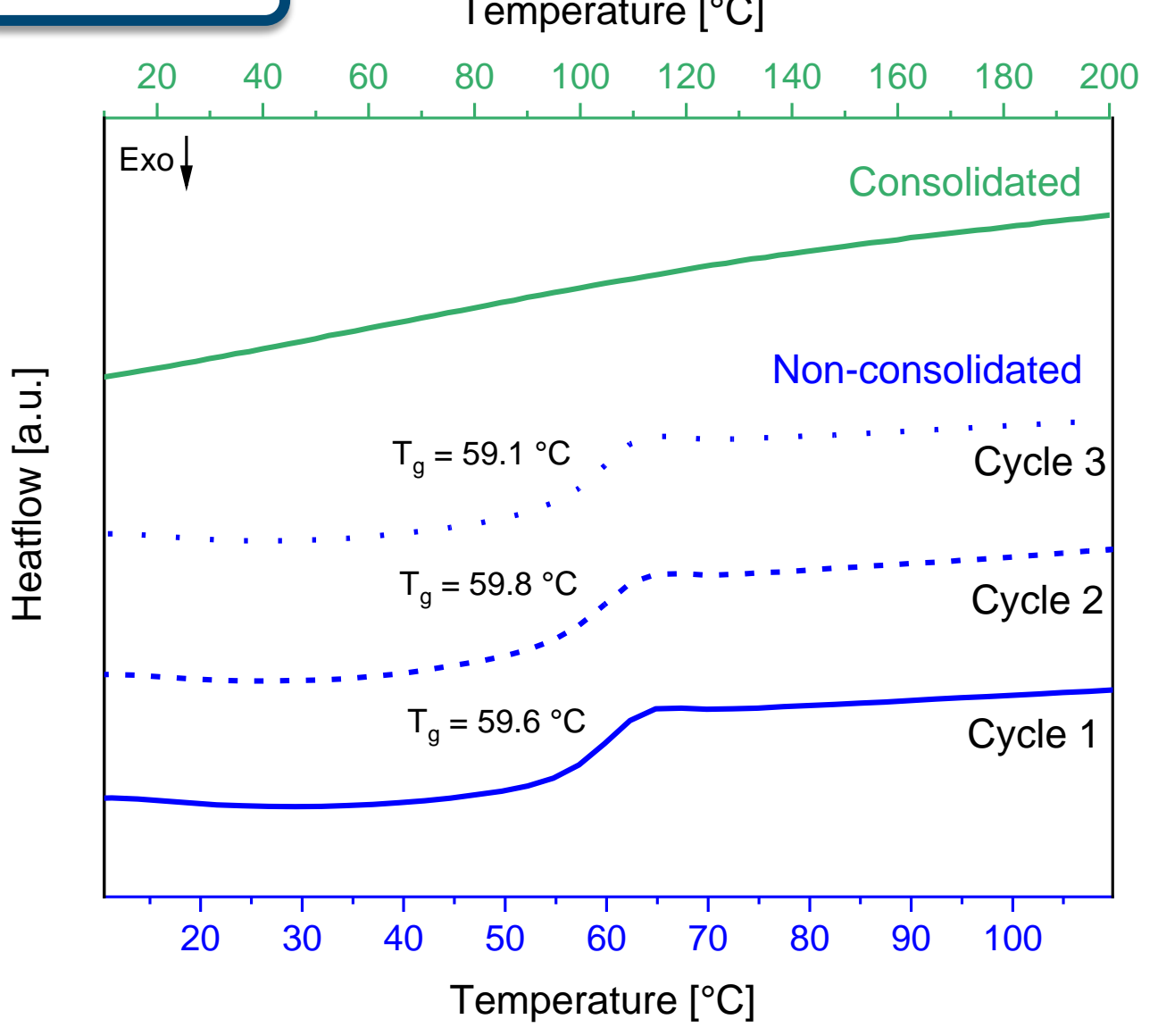
### TGA



### SEC



### DSC



## References

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