Synthesis and Characterization of Polysilsesquioxane Hybrid Melting Gels

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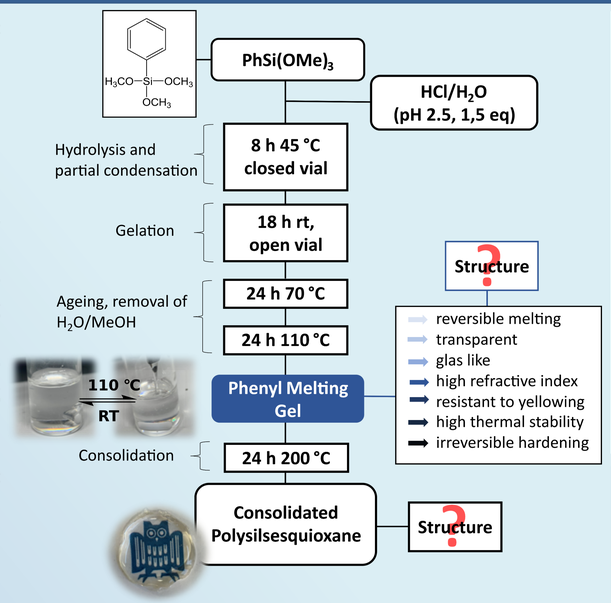
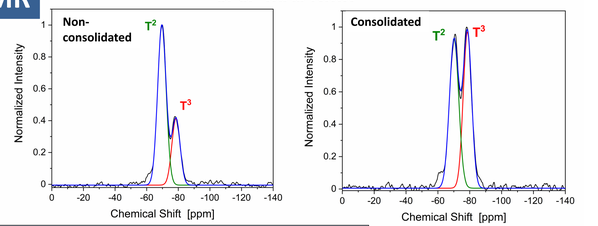
Melting gels are inorganic-organic compounds with siloxane and silsesquioxane units produced by a combined hydrolysis and condensation reaction of di- and trialkoxysilanes.[1] They are rigid, transparent materials at room temperature and soften reversibly around 110 °C. Exposure to a consolidation temperature above 150 °C results in irreversible curing to a glassy, transparent, insoluble, and thermoset material. 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.[2]



NMR

^{29}Si CP-MAS NMR



	T^2 [%]	T^3 [%]	DC [%]	OMe [%]*	OH [%]
Non-consolidated	71	29	76	10	14
Consolidated	51	49	83	< 10	<14

*By integration of the liquid ^{1}H-NMR and comparison of the intensities of the ^{13}C CP-MAS NMR

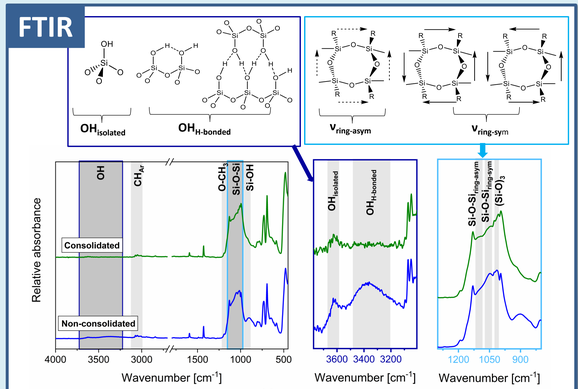
$$DC\,[\%] = \frac{T^3[\%]\cdot 3 + T^2[\%]\cdot 2}{3}$$

$$OH\,[\%] = 100\% - DC\,[\%] - MeO[\%]$$

DC = degree of condensation
OH = remaining hydroxy groups

- T^2, T^3 units → complete integration of the trimethoxysilane, still non-condensed OMe- and OH-groups
- Thermal curing leads to higher cross-linking → no softening, insolubility

FTIR



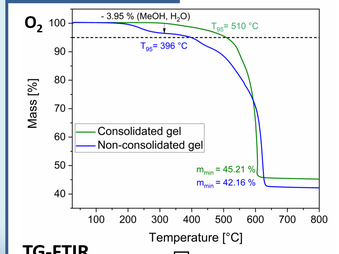
- H-bonded and isolated OH groups[5] → important for melting gel behaviour
- Broad complex Si-O-Si band (1050-1000 cm^{-1})[6]

→ different silsesquioxane species
→ 1050 cm^{-1} low-symmetric structures: random network
→ 1100 cm^{-1} symmetrical species: ladders, cycles, cages

- After consolidation: more cross-linked structure, increase in symmetric structural units

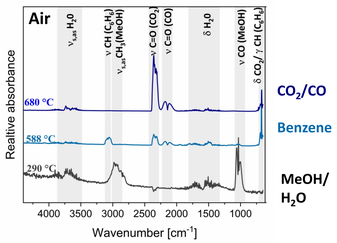
TG/TG-FTIR

(T^{95}= Temperature measured at the point of 95% weight loss)



TG-FTIR

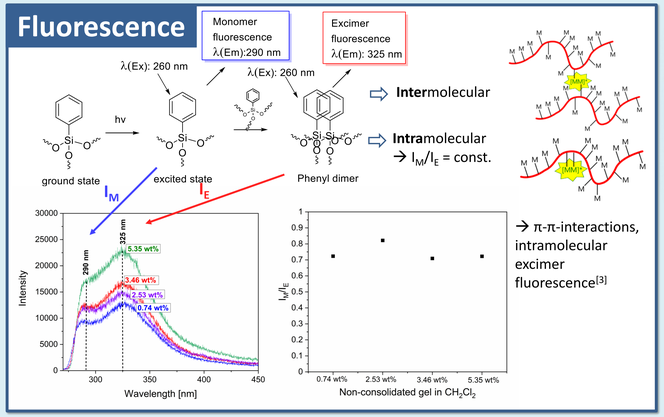
Non-consolidated gel



→ consolidation = further condensation reactions
→ high thermal stability (T_{95}≈ 500 °C)

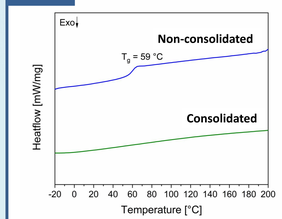
Characterization

Fluorescence



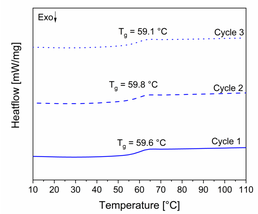
→ π-π-interactions, intramolecular excimer fluorescence[3]

DSC



- No T_g after consolidation

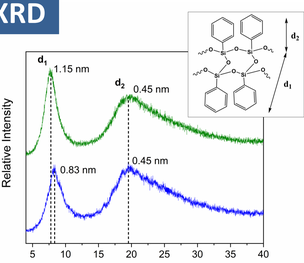
→ additional crosslinking, no softening behaviour



- After three heating cycles (0-110 °C) no change of T_g

→ no further crosslinking
→ reversible softening

XRD

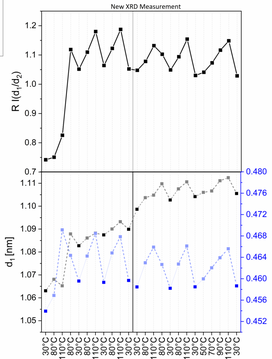


	Non-consolidated gel	Consolidated gel
d_1 [nm]	0.83	1.15
d_2 [nm]	0.45	0.45
R= I(d_1)/I(d_2)	0.98	1.15

- Structure with ladder domains[4]

→ increased after consolidation by a reorientation of the siloxane chains and an inter- and intramolecular condensation of -OMe and -OH groups

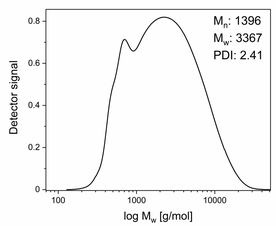
XRD - reversibility studies



- Reversible melting process under defined heating and cooling conditions

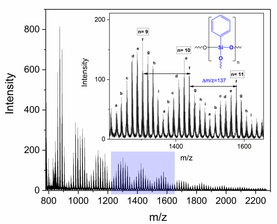
SEC/MALDI-TOF

SEC



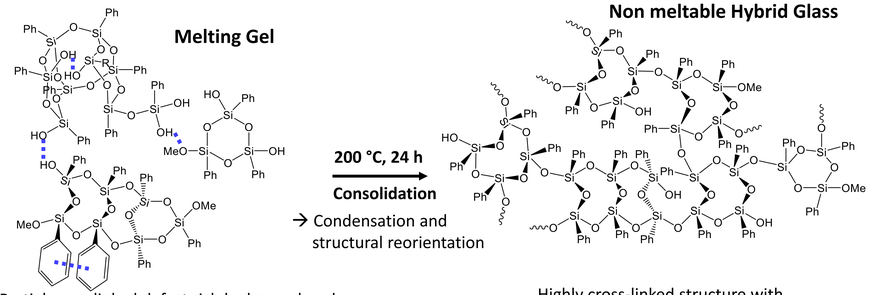
*RI detector, PS standard, THF

MALDI-TOF



→ low molecular weight

Conclusion



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

Highly cross-linked structure with ladder domains

References

[1] Jitianu, G. Amatucci, L. C. Klein, *J. Am. Ceram. Soc.* **2009**, *92*, 36-40.
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