Influence of organic substituents on the structure and properties of polysilsesquioxane melting gels

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INTRODUCTION

Polysilsesquioxanes, polycondensation reaction prepared from via а organoalkoxysilanes, can form glass-like, hard, and transparent materials that can be reversibly softened at 110 °C. A temperature increase above the softening point leads to the formation of covalent bonds between previously stabilized hydroxy and alkoxy groups and irreversible curing.¹ This class of materials is also known as melting gels. Due to the high transparency, high thermal stability, a variable refractive index and adjustable viscosity, the materials are interesting for many applications, for example, in the optoelectronic field.² The softening properties are particularly well known in glasses synthesized from trialkoxy- and dialkoxysilanes with phenyl and methyl groups as organic compounds.³ In terms of temperaturedependent, thermoplastic and duroplastic properties, we investigated the influence of various aryl substituents (1-naphthyl, 2-naphthyl, phenanthrenyl) and alkyl substituents (ethyl to octadecyl) on the formation of polysilsesquioxane-melting gels.





Synthesis



 $|\mathsf{T}^2|$

T³

PSQ

2-NpPSQ

1-NpPSQ

HexPSC

OctPSC

DecPSQ

-80

(a.u.)

Normalized intensity

-90

6

2-NpPSQ_T

INpPSQ_T

HexPSQ_T

OctPSQ₊

DodecPSQ-

2 DecPSQ

Defined cubic

species

 $|\mathbf{T}^1|$

Characterization





²⁹Si NMR

- $DC(1-Np) < DC(2-Np) \rightarrow \text{lower steric}$ hindrance of 2-Np group increase hydrolysis and condensation rate
- $DC(Alkyl) > DC(Aryl) \rightarrow hydrophobic$ interactions > steric hindrance Thermal treatment:
- Further condensation reactions. • Hex-, Oct-, Dec: intramolecular condensation reactions lead to the formation of defined cubic units \rightarrow avoid building of a dense network





- Highly disordered amorphous structure, with a ladder-like or layer-like composition of the silsesquioxane units⁶
- Increase in d₁ (distance between chains) with increasing chain length Thermal treatment:
- Np, Me, Et: increase in $d_1 \rightarrow$ more ordered structure⁷
- **Hex-Dodec:** decrease in $d_1 \rightarrow$ more disordered structure
- **Dec, Dodec:** phase transition at -50, -20 °C = crystallisation of alkyl chains⁸

CONCLUSION

The acid catalyzed polycondensation reaction of phenyltrialkoxysilanes leads to a material with a thermoplastic and a thermoset temperature regime based on the stabilization of silanol groups in the material. Depending on the alkyl chain length, solid materials with a dense network structure (C1–C4), which were no longer softenable, viscous liquids with cage-like motifs (C6, C8, C10), and waxy materials with lamellar layered structures (C10, C12, C16, C18), which were not curable, were formed. Missing stabilization of the OH groups and self-assembly phenomena, which favor the cage and semicrystalline layer formation were detected in the resulting materials, which leads to the loss of the typical melting gel properties.⁹ In contrast, trialkoxysilanes with naphthyl substituents formed melting gel-like, transparent, glassy and reversibly softenable materials. The isomerism of the naphthyl group was shown in a different condensation degree and loss of the softening behavior after thermal treatment only with the 2-Np group. The sterically more demanding 1-Np group lowers the hydrolysis and condensation rate and caused in a lower network formation and no irreversible curing. The presence of groups in trialkoxysilanes that inhibit self-assembly and the formation of ordered structures, but also lower the degree of condensation due to steric hindrance is an essential factor in stabilization of OH groups and therefore the softening properties of polysilsesquioxanes. Aromatics in particular have proven to be ideal moieties for the formation of melting gels due to their steric demand and aromatic rigidity.



(a.u.)

nalized intensity

Nor

-40



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 T^2

T¹

-60

Chemical shift (ppm)

T³

 $\mathsf{PSQ}_{\mathsf{T}}$

-90

-80

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