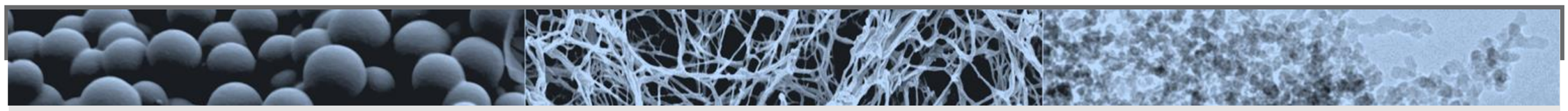
Hydrophobization of resorcinol-formaldehyde xerogels



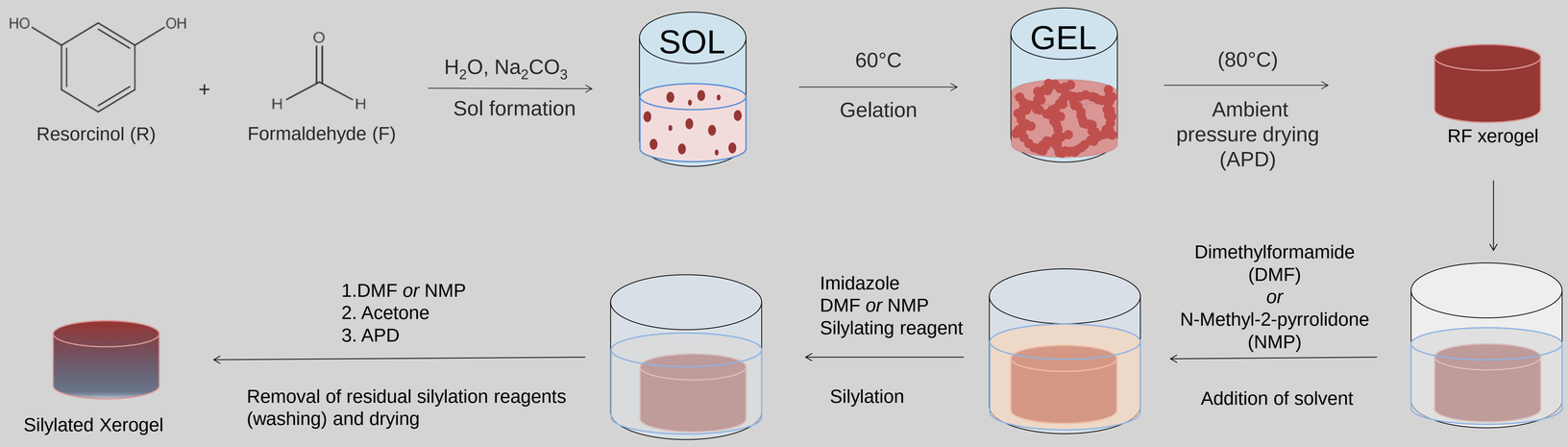
Motivation

The chemical modification of xerogels at their surface can drastically change their properties. While silylation using trimethylsilyl chloride is routinely applied to silica gels on an industrial scale, only few examples of a silylation of organic gels such as resorcinol-formaldehyde (RF) xerogels are known, and these are basically restricted to trimethylsilyl and related unhindered moieties.[1-3] RF gels are inherently hydrophilic due to the presence of phenolic hydroxyl groups. However, a chemical modification can cause them to become hydrophobic.
We have investigated the silylation of resorcinol-formaldehyde gels in solution using a number of sterically demanding silyl reagents and amine bases.

Hydrophilic RF xerogel

Experimental

Synthesis of silylated RF xerogels



- Silylation in solution phase
- Addition of external base
- Use of sterically demanding silylating reagents
- Variation of Si-counterion (electronically activated triflate)

Silylating reagents:

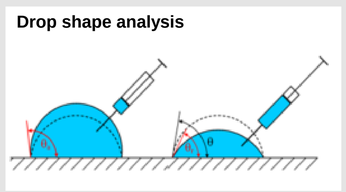
Trimethylchlorsilane (TMS-Cl)
tert.-Butyldimethylchlorsilane (TBS-Cl)
tert.-Butyldiphenylchlorsilane (TBDPS-Cl)
Triisopropylsilyltriflate (TIPS-OTf)
Triisopropylsilylchloride (TIPS-Cl)

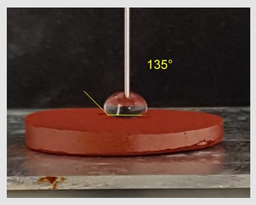
Characterization & Results

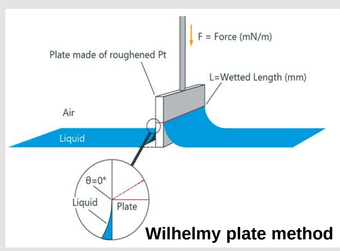
Measurement of static contact angle
- using a cannula, the deposited drop of water was enlarged and the contact angle was determined by the tangent method

Measurement of dynamic contact angle
- The solid sample is immersed in a liquid with known surface tension. The contact angle can be calculated from the measured force by transposing the Wilhelmy equation

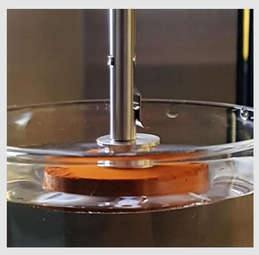
➢ Hydrophobization of RF sample treated with TMSCl is not successful
➢ all other used silylation agents are showing long-term hydrophobic characteristics



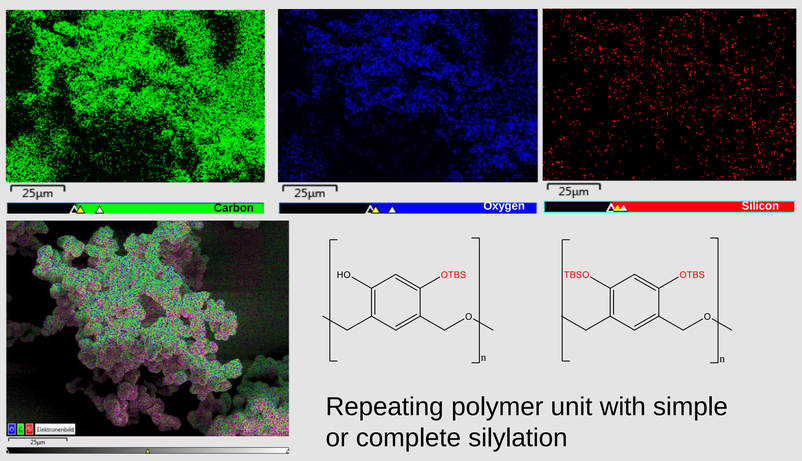




Wilhelmy plate method



Silylated RF with	Static Contact Angle [°]		Dynamic Contact Angle [°]	
	Determination by tangent method		Solid state contact angle method according to Wilhelmy	
Exposition time to air	2 months	6 months	2 months	6 months
TBS-Cl	136.77 ± 1.73	135.00 ± 1.73	120.80 ± 13.73	136.10 ± 2.80
TBDPS-Cl	138.27 ± 1.77	139.03 ± 2.27	106.43 ± 18.80	131.03 ± 5.87
TIPS-OTf	142.22 ± 1.67	141.77 ± 1.63	138.00 ± 6.66	139.97 ± 5.73
TIPS-Cl	142.77 ± 1.47	141.10 ± 0.63	153.20 ± 7.03	146.23 ± 7.63



Repeating polymer unit with simple or complete silylation

SEM-EDX-Characterization

Left: SEM-EDX images of an RF xerogel treated with TBSCl

The EDX measurement shows a silicon content of approx. 0.66%. This value corresponds to a degree of silylation of almost 5%.

➢ Considering the observed contact angles it can be assumed that even this low degree of silylation is sufficient to render the entire monolith hydrophobic

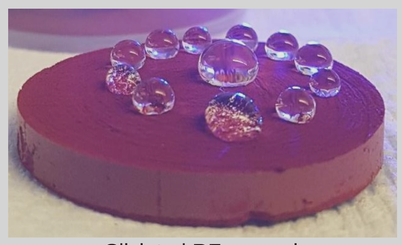
Sample	C [Mass.%]			O [Mass.%]			Si [Mass.%]		
	theo. simple	theo. complete	exp.	theo. simple	theo. complete	exp.	theo. simple	theo. complete	exp.
Untreated RF	/	66.67	63.97	/	33.33	36.03	/	/	/
Silylated RF (TBS)	68.85	69.77	65.07	19.67	13.95	32.71	11.48	16.28	0.72
Silylated RF (TIPS)	72.86	75.00	67.32	17.14	11.54	32.02	10.00	13.46	0.66

Conclusion

➢ Development of a synthetic methodology for the silylation of resorcinol-formaldehyde-xerogel monoltihs

➢ Sterically and electronically varied silyl reagents can be applied in solution phase using auxilary amines as external base

➢ Wetting studies indicate long-lasting hydrophobicity effects of silylated RF-xerogels



Silylated RF xerogel

References

[1] M. A. Aegerter, N. Leventis, M. M. Koebel, *Aerogels Handbook*, Springer New York, **2011**.
[2] S. Schwarz, *Organic gels, US6288132B1*, E. I. du Pont de Nemours and Company, U.S.A., **2001**.
[3] I. D. Alonso-Buenaposada, M. A. Montes-Morán, J. A. Menéndez, A. Arenillas, *Reactive and Functional Polymers* **2017**, *120*, 92-97.

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