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Tuning the Properties of Phenolic Aerogels by Derivatization of Phenolic Precursors

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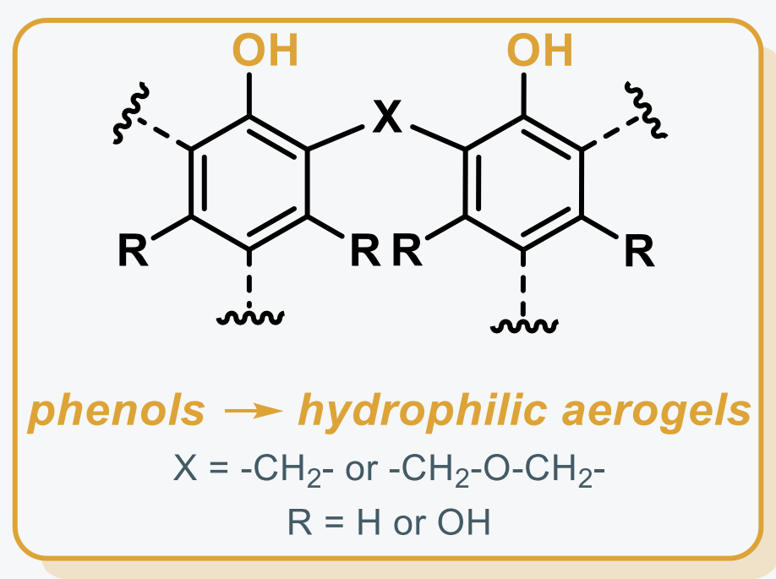
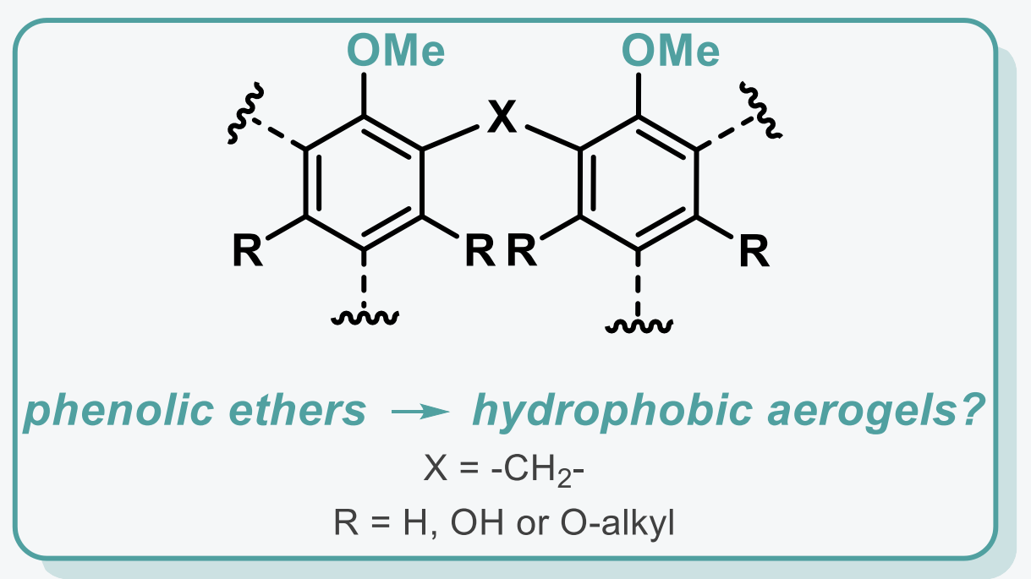
Motivation & Background

Organic aerogels are open-porous nanostructured solids obtained by gelation-polymerization processes followed by drying of the resulting wet gels. The most prominent example is based on resorcinol-formaldehyde (RF), as it is an highly efficient thermal insulator.[1] However, the phenolic nature of RF renders the material hydrophilic, a factor that partly limits its commercialization.[2] In order to address this issue, we studied the condensation of various commercial and readily available less polar alkoxy phenols and methoxybenzenes with formaldehyde to yield inherently hydrophobic aerogels.



phenols → hydrophilic aerogels

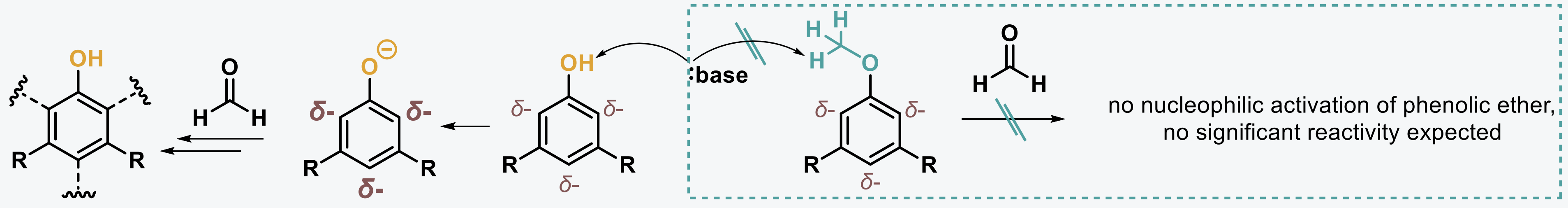
X = -CH_2- or -CH_2-O-CH_2-
R = H or OH



phenolic ethers → hydrophobic aerogels?

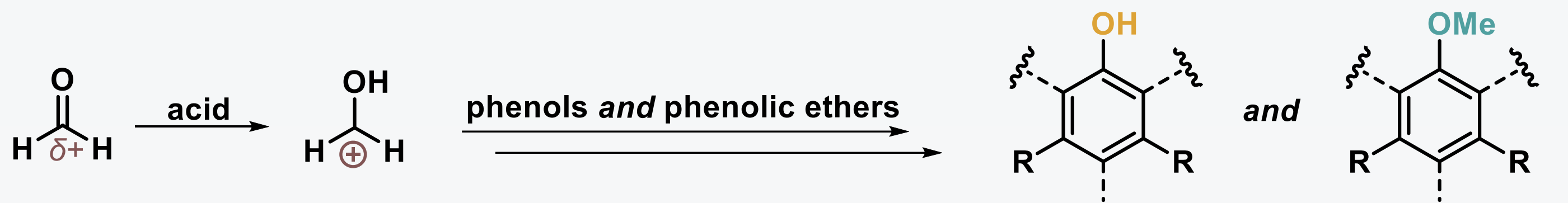
X = -CH_2-
R = H, OH or O-alkyl

Increased *nucleophilicity* of the *phenolic* component under *basic* conditions:



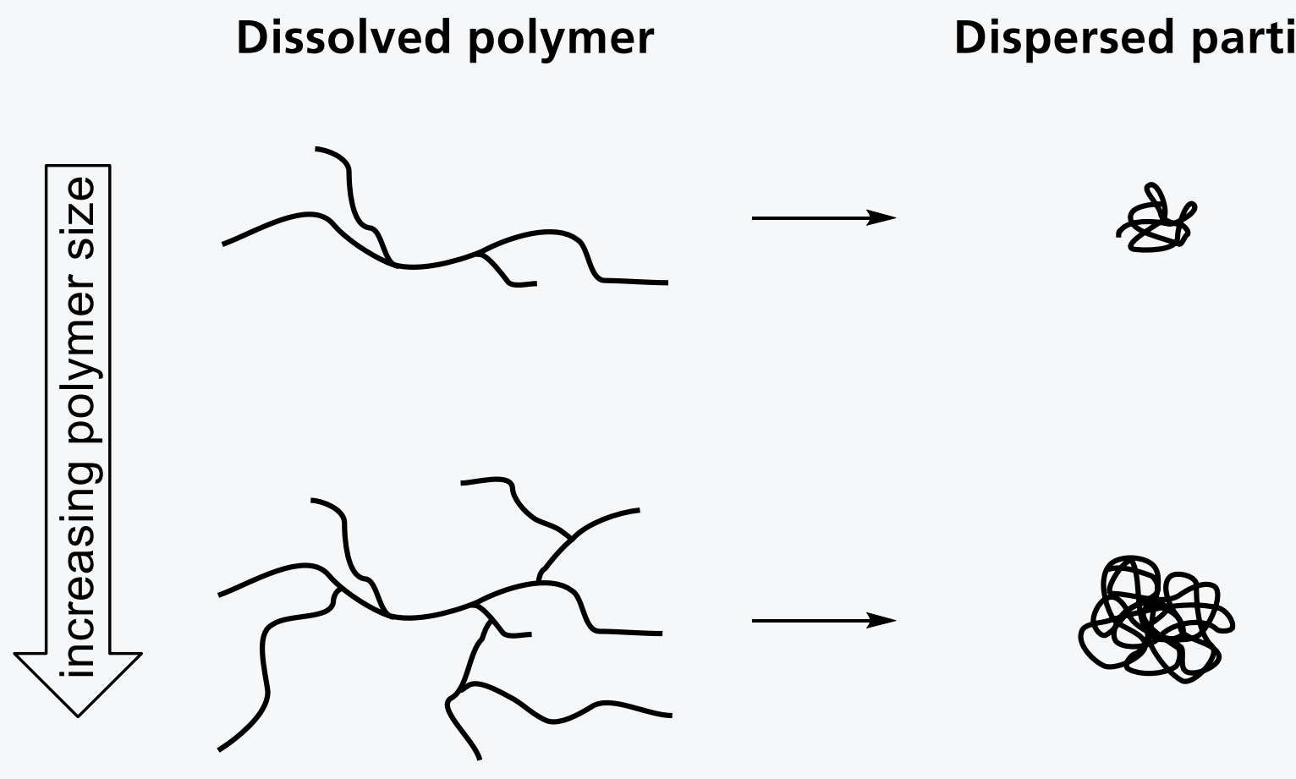
no nucleophilic activation of phenolic ether, no significant reactivity expected

Increased *electrophilicity* of the *aldehyde* component under *acidic* conditions:



electrophilic activation of aldehyde, significant reactivity expected

Considering the mechanisms of base- and acid catalysis, we hypothesize that base catalysis is not suitable for phenolic ethers and that activation of the aldehyde with an acid should be feasible.[3]



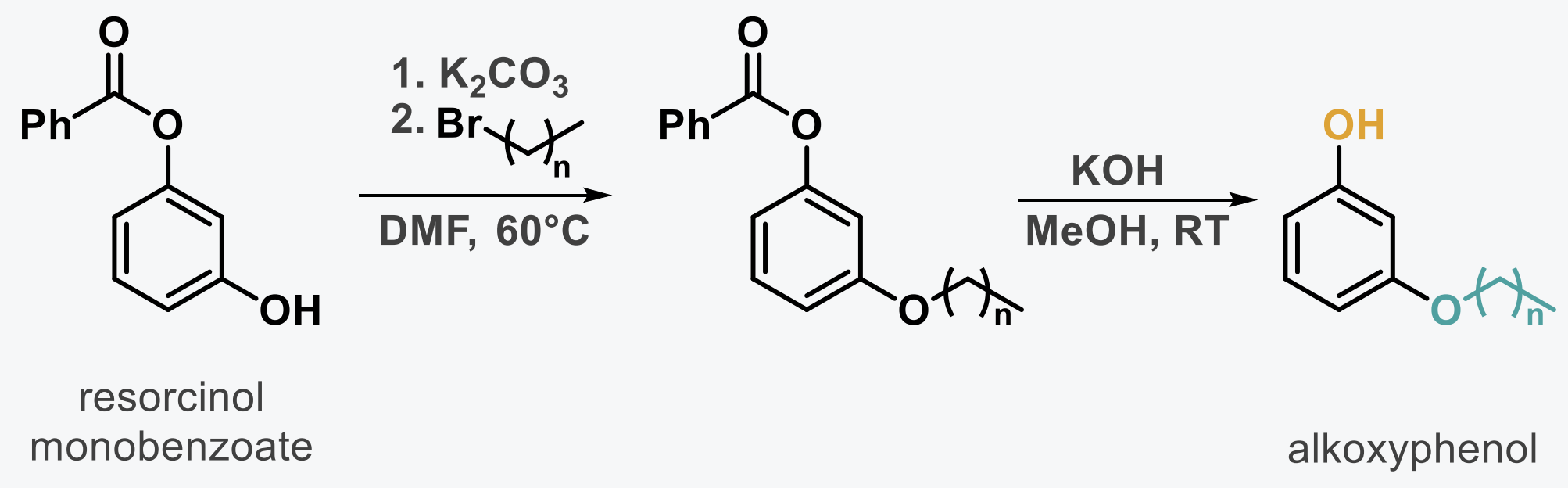
low-solubility solvent, early transition = small particles = high surface area

high-solubility solvent, late transition = big particles = low surface area

We use Hansen solubility parameters as quantitative descriptors of solvent properties and correlate them to the surface areas of the aerogels synthesized in various solvents.[4]

Experimental

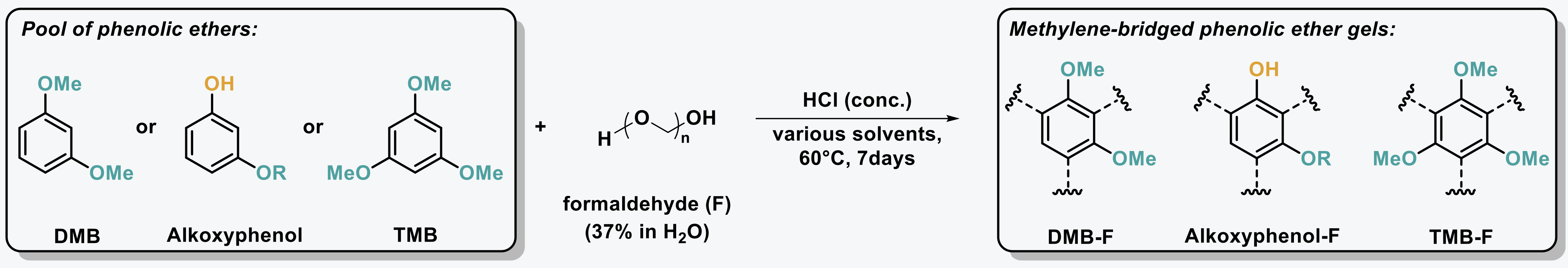
Synthesis of 3-alkoxyphenols[5]

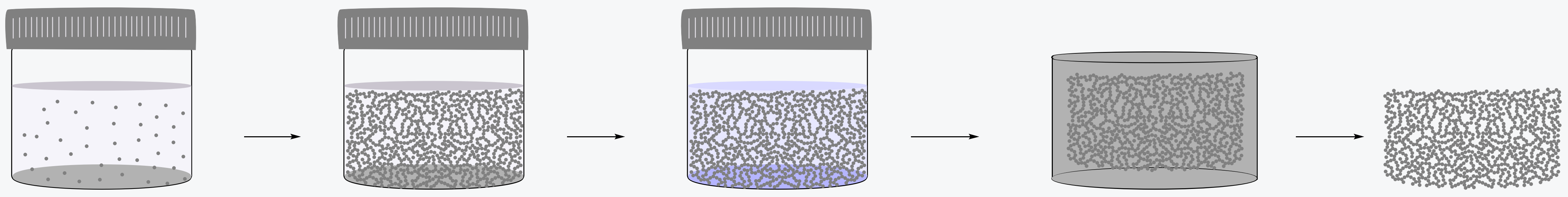


n =	3-alkoxy phenol	yield [%]
0	MeO-phenol	-[a]
1	EtO-phenol	72
2	PrO-phenol	60
3	BuO-phenol	81
4	PeO-phenol	75
5	HxO-phenol	76

[a] commercially available

Synthesis of phenolic ether - formaldehyde aerogels





polymerization
formation of nm - µm sized particles

gelation and aging
formation and stengthening of the interpenetrating network

washing with EtOH
exchange of the synthesis solvent to a solvent miscible with supercritical CO_2 (sc-CO_2)

sc-CO_2 drying of the gels
exchange of EtOH with sc-CO_2 followed by transition of sc-CO_2 to CO_2 gas by depressurization of the autoclave

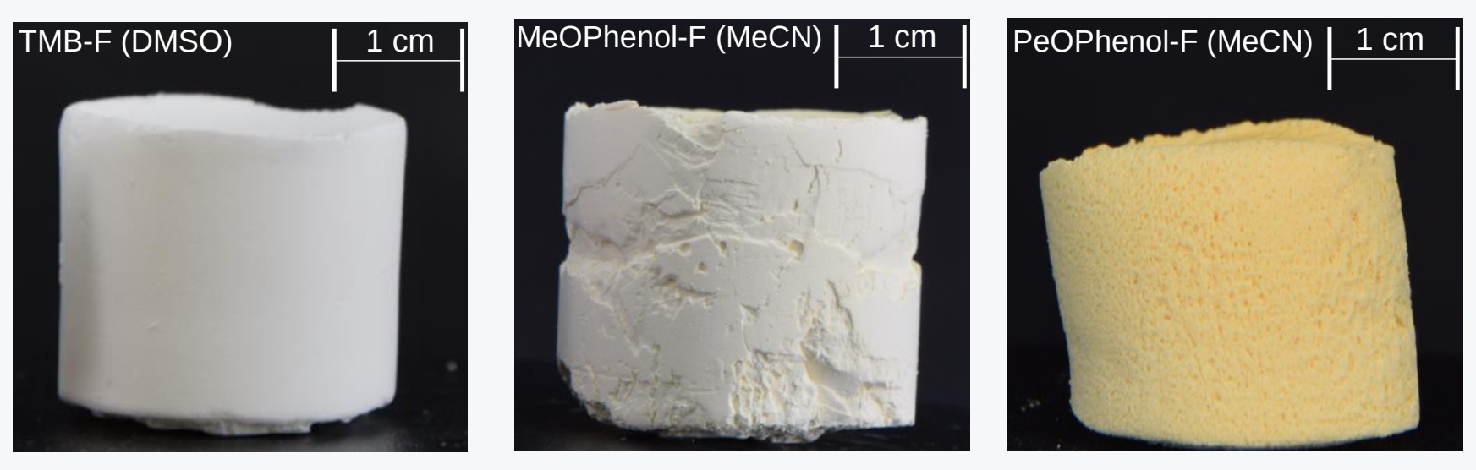
aerogel

Results

Acid-catalyzed gelation of TMB and alkoxyphenols with formaldehyde

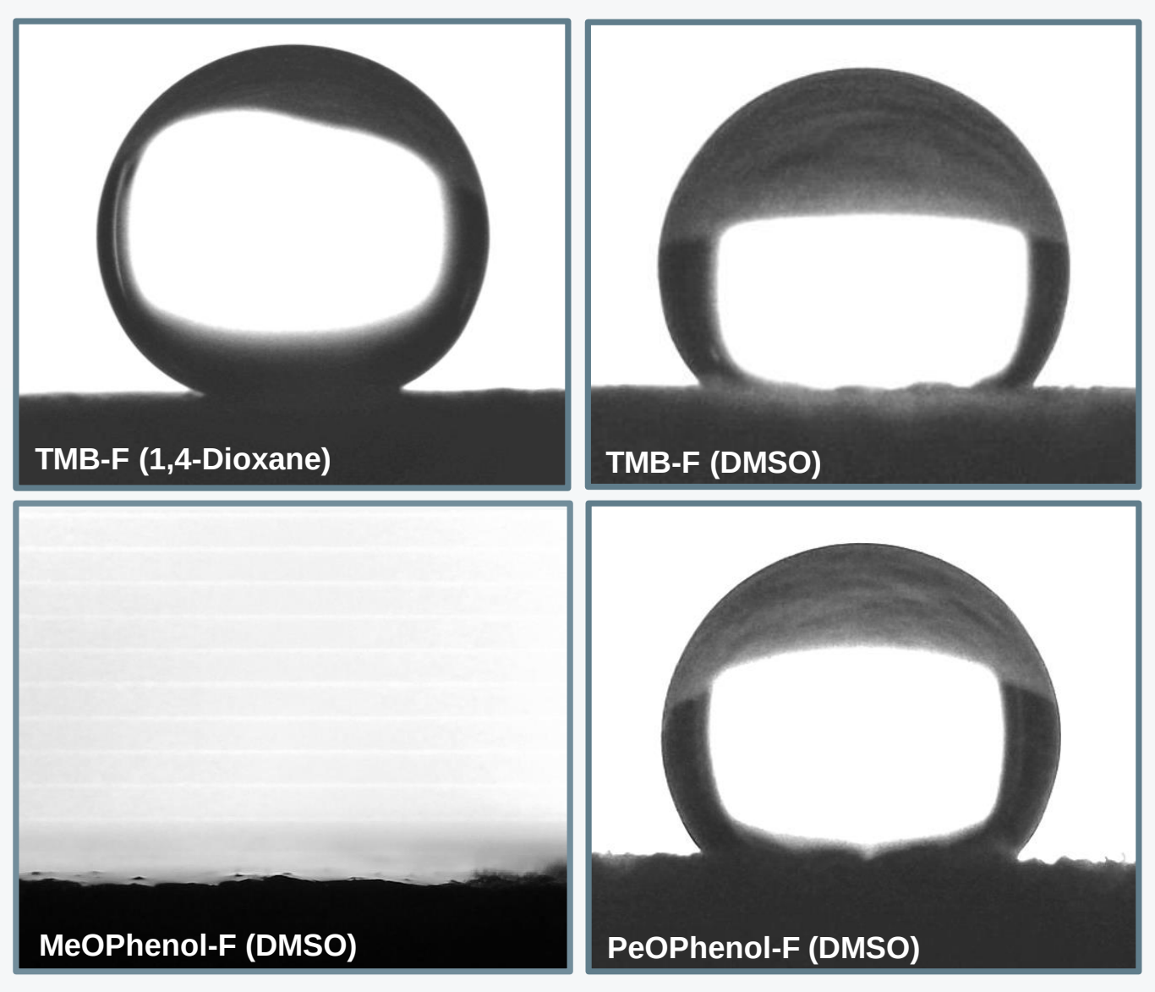
Material	Gelled in
DMB-F	-[a]
TMB-F	1,4-Dioxane, DMSO, MeCN, AcOH
MeOPhenol-F	1,4-Dioxane, MeCN, AcOH
EtOPhenol-F	-
PrOPhenol-F	-
BuOPhenol-F	-
PeOPhenol-F	DMSO
HxOPhenol-F	-[a]

[a] precipitates were obtained instead of gels



- ○ Envelope density: TMB-F = 0.13 – 0.30 g/cm^3
  MeOPhenol-F = 0.11 – 0.40 g/cm^3
  PeOPhenol-F = 0.16 g/cm^3
- ○ Porosity: TMB-F = 77 – 99 %
  MeOPhenol-F = 59 – 92 %
  PeOPhenol-F = 86 %
- ○ BET surface area: TMB-F = 1 – 284 m^2/g
  MeOPhenol-F = 5 – 428 m^2/g
  PeOPhenol-F = 0.5 m^2/g
- ○ All materials are meso- & macro-porous.

Wetting behavior – water contact angles

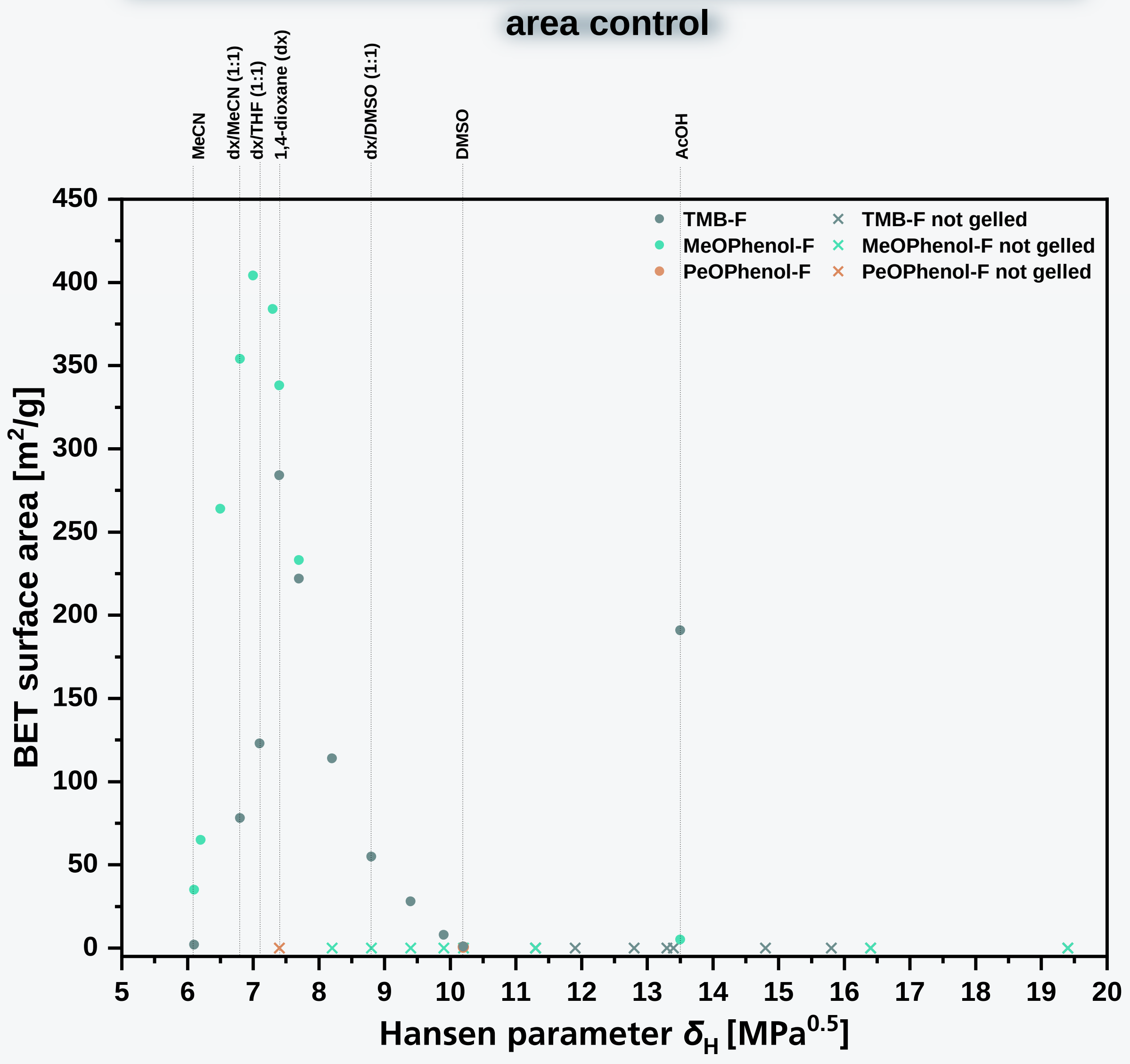


Material	Gelled in	Contact angle [°]
TMB-F	1,4-Dioxane	151 ± 3
TMB-F	DMSO	127 ± 5
TMB-F	AcOH	153 ± 2
TMB-F	MeCN	-[a]
MeOPhenol-F	1,4-Dioxane	-[a]
MeOPhenol-F	MeCN	-[a]
MeOPhenol-F	AcOH	-[a]
PeOPhenol-F	DMSO	132 ± 4

[a] water droplets are soaked up

- ○ TMBF aerogels are (super-)hydrophobic.
- ○ MeOPhenol-F aerogels soak up water.
- ○ PeOPhenol-F aerogel is hydrophobic.
- ○ Contact angle increases with finer pore structure.

Hansen solubility parameters as guiding tool for surface area control



- ○ Inner surface area correlates with δ_H (H-bonding).
- ○ Due to free –OH, MeOPhenol-F requires solvents with smaller δ_H for gelation than TMB-F.
- ○ Solubility of alkoxyphenol-F in DMSO decreases with increasing length of the alkoxy substituent.
- ○ Partial acetylation (confirmed by ^{13}C CP-MAS NMR and IR) of methylol goups in AcOH leads to different polarity of the polymers.
- ○ No correlation for δ_D (dispersive) and δ_P (dipole).

Conclusion

- ○ Acid-catalysis is feasible for the gelation of phenolic ethers with formaldehyde. Aerogels were obtained using 1,3,5-trimethoxybenzene, 3-methoxyphenol and 3-pentoxyphenol as phenolic component in various solvents.
- ○ The resulting materials were shown to be (super-)hydrophobic. The contact angles are furthermore influenced by the microstructure.
- ○ The δ_H Hansen parameters of solvents were shown to correlate with the surface areas of the aerogels which enables them as a tool for tuning of the microstructure.

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