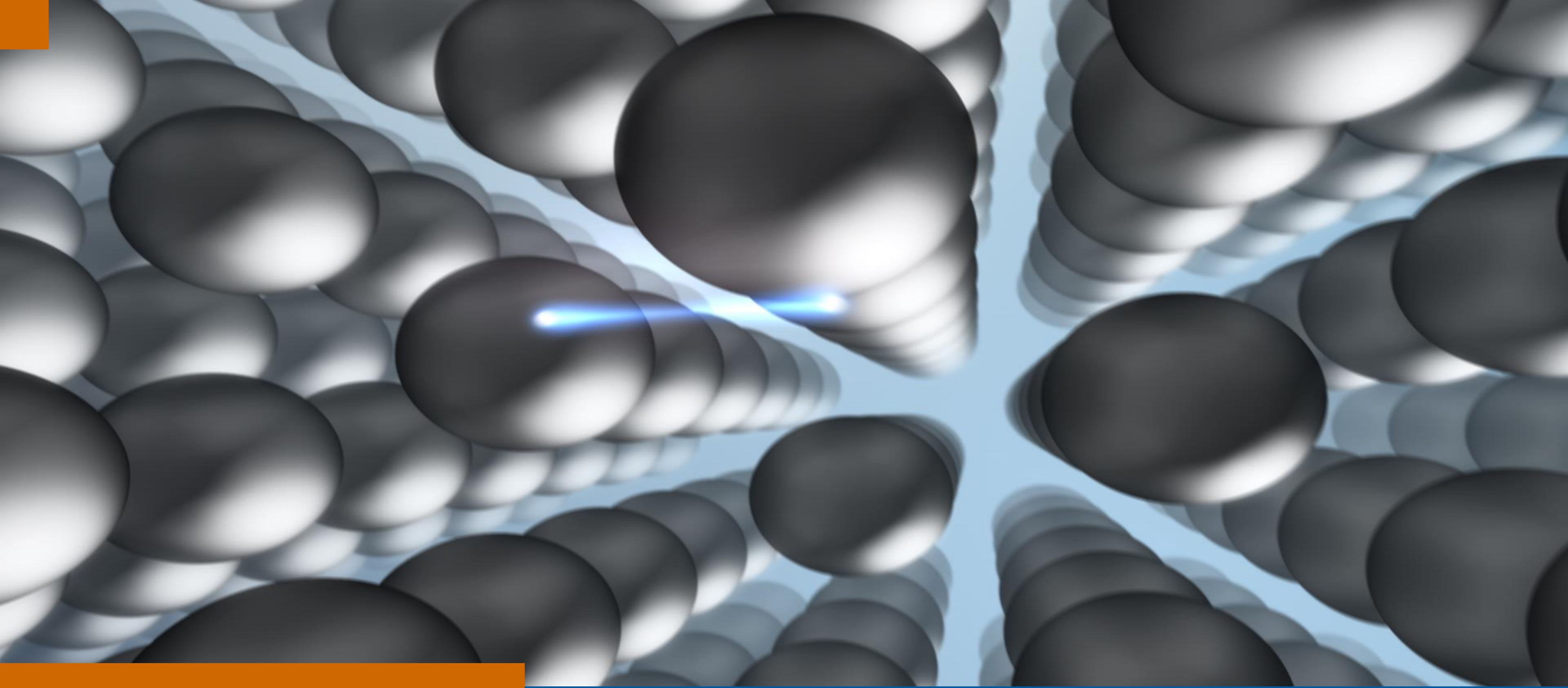


Comparative evaluation of porous PMO materials by PAS and EP

A. G. Attallah, A. S. Vishnevskiy, M. O. Liedke, E. Hirschmann, M. Butterling, D. S. Seregin, A. A. Rezvanov, K. A. Vorotilov, M. R. Baklanov, and A. Wagner

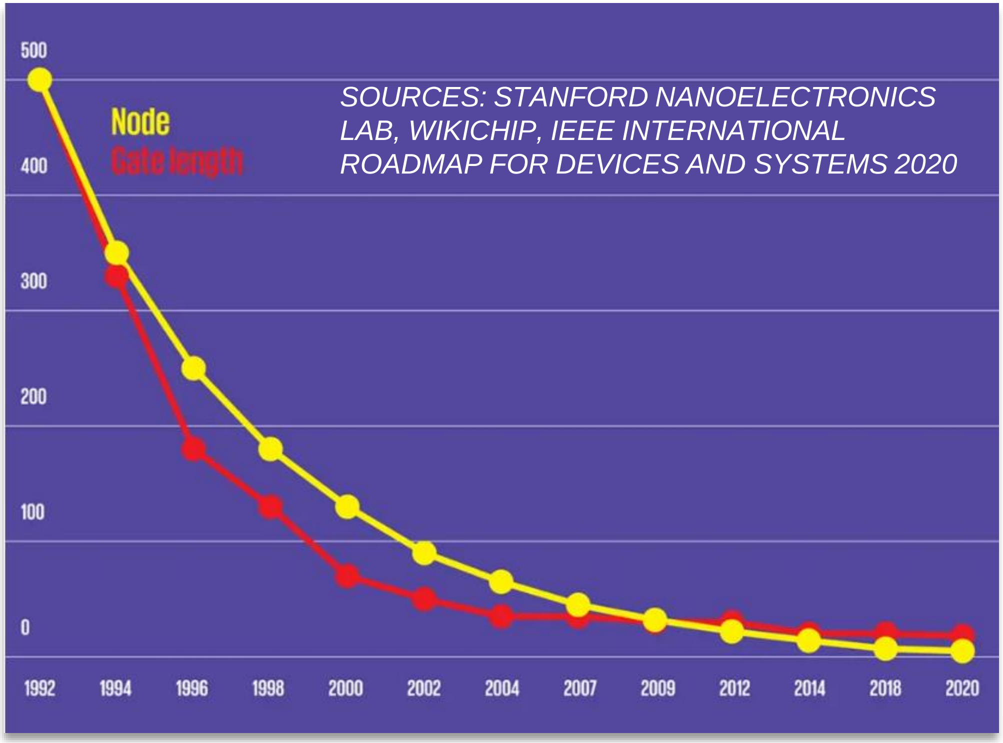
Partner von DRESDEN concept exzellenz-dresden.de

HZDR

HELMHOLTZ ZENTRUM DRESDEN ROSSENDORF

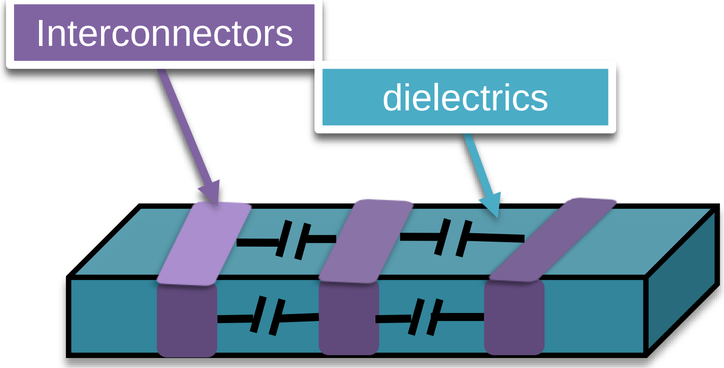
Contents

Low – k dielectrics – the topic

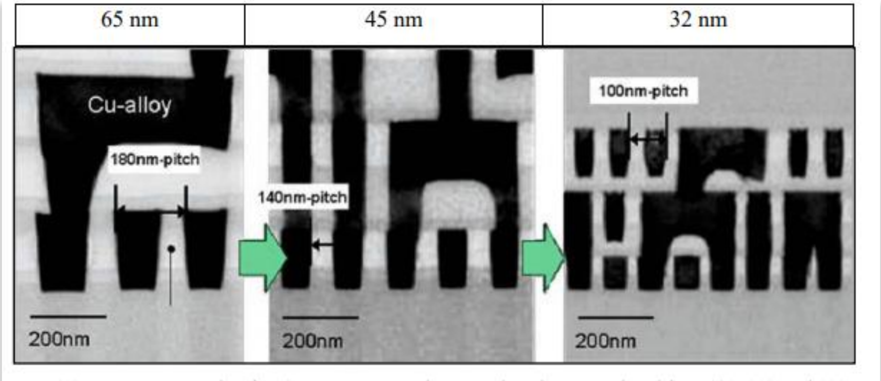


SOURCES: STANFORD NANOELECTRONICS LAB, WIKICHIP, IEEE INTERNATIONAL ROADMAP FOR DEVICES AND SYSTEMS 2020

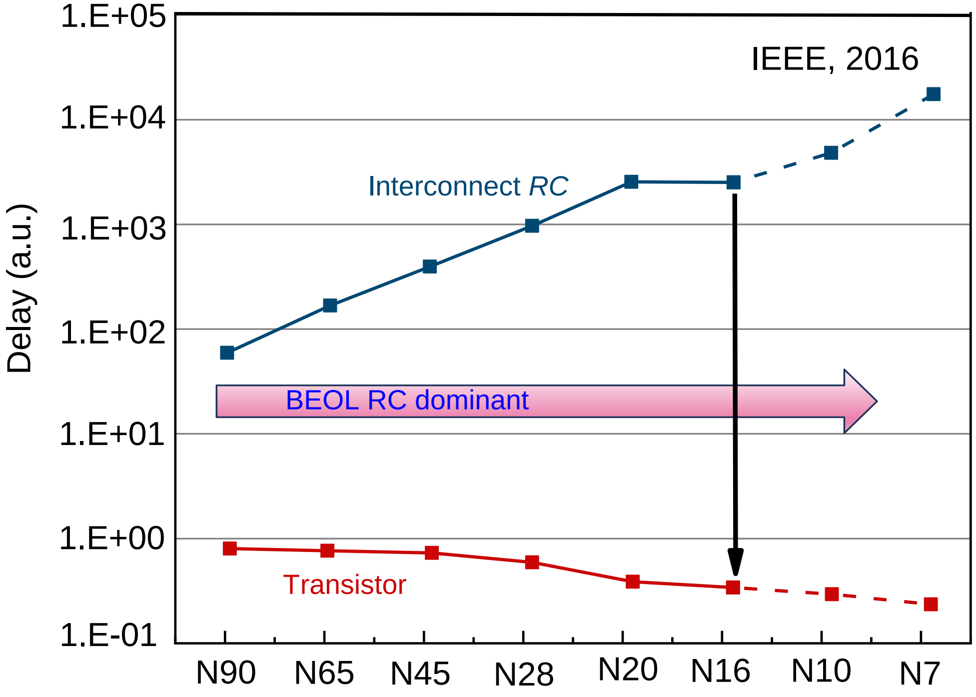
- Scaling down:
  - \- Capacitance (*C*) increases
  - \- Resistance *(R)* of metal connectors
  - \- *RC* delay increases



Pradeep Kumar Singh, Ph.D. thesis, Chemnitz, 2013



Low – k dielectrics – the topic

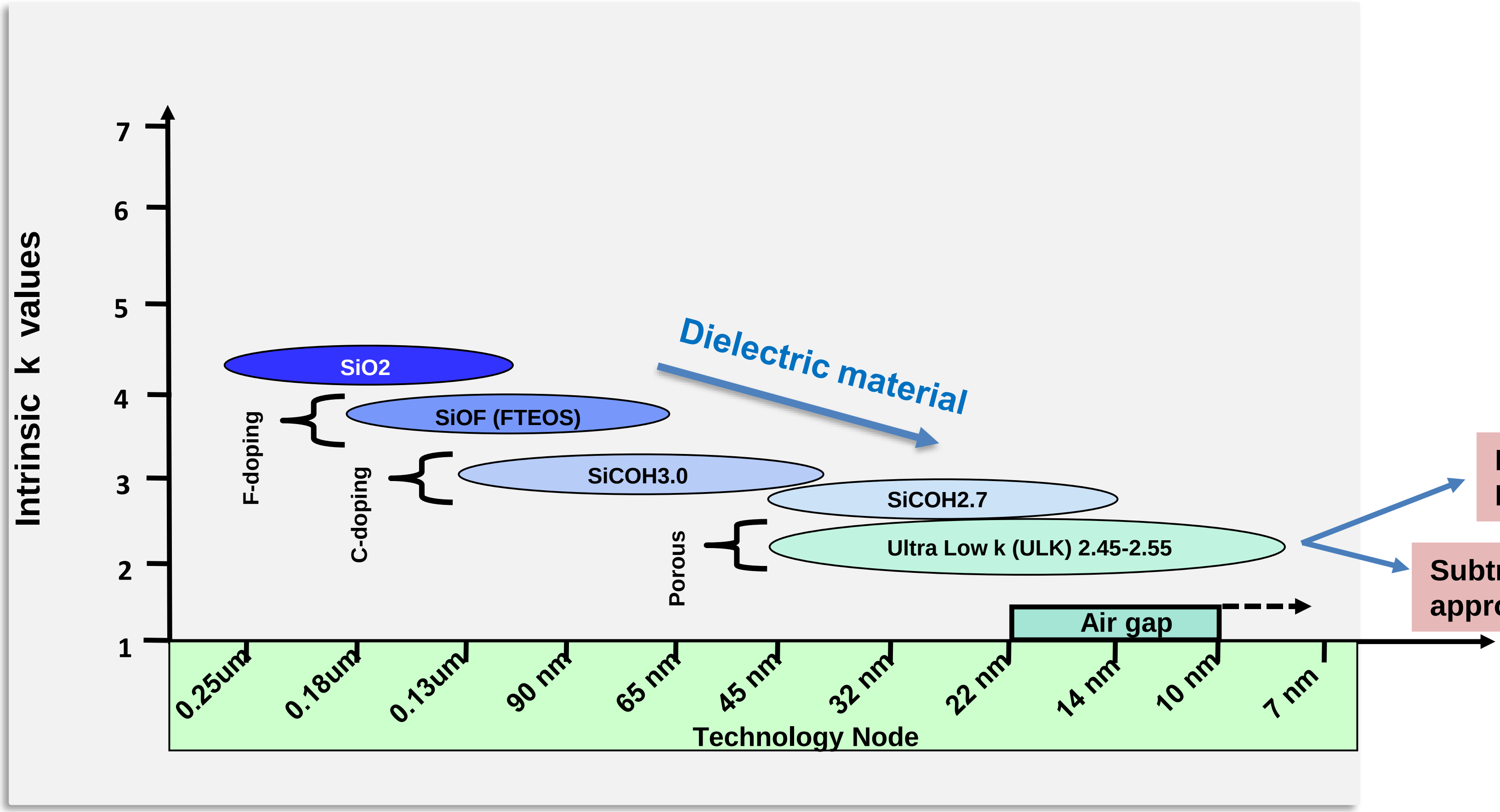


Challenge: reduction of signal delay, *RC*

Metal research

Low-k dielectrics research

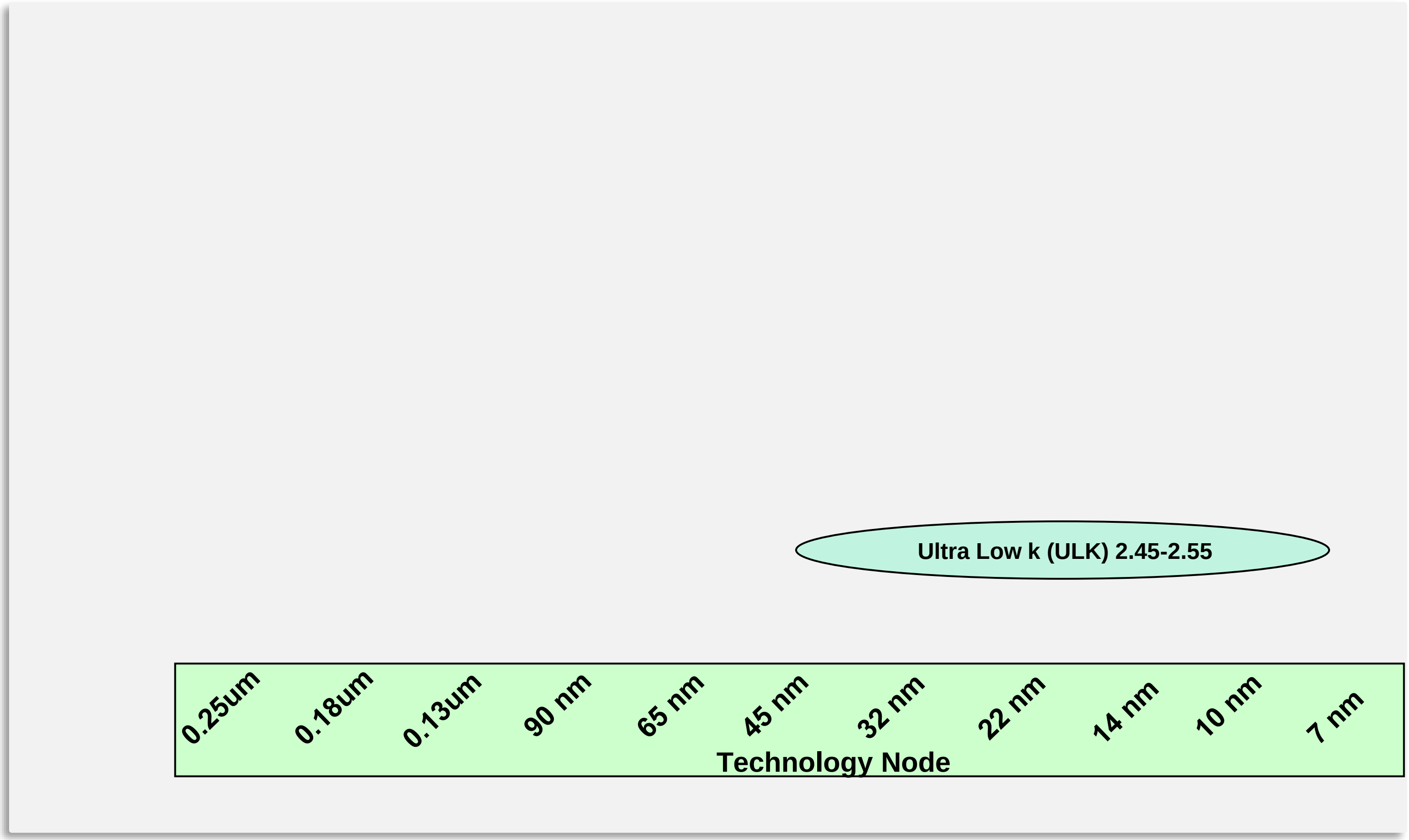
Low – k dielectrics – strategies



Low PID SiCOH K=3.0

Subtractive approach, k=2.2-3.0

Ultra - low – k dielectrics



Subtractive approach, k=2.2-3.0

Motivation

Aim

Preparing efficient ULK

How?

k decreases by pore creation & grafting organic groups in SiO_2

Challenge

Improving the poor mech. stability

Methodology

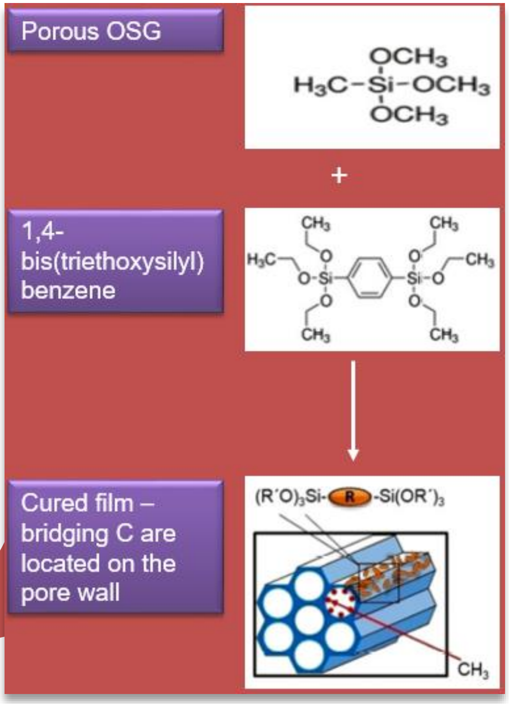
Replacement of O_2 in SiO_2 by carbon-based bridges (higher regidity)

Side effect

The new structure is not completely hydrophopic

Improvement?

Terminal methyle groups enhance the hydrophobicity



Porous OSG

1,4-bis(triethoxysilyl) benzene

Cured film – bridging C are located on the pore wall

A. S. Vishnevskiy et al., Materials 2020, 13

Work plan

Varying the C-bridge / methyl terminal

ratio at a fixed porogen content

Motivation

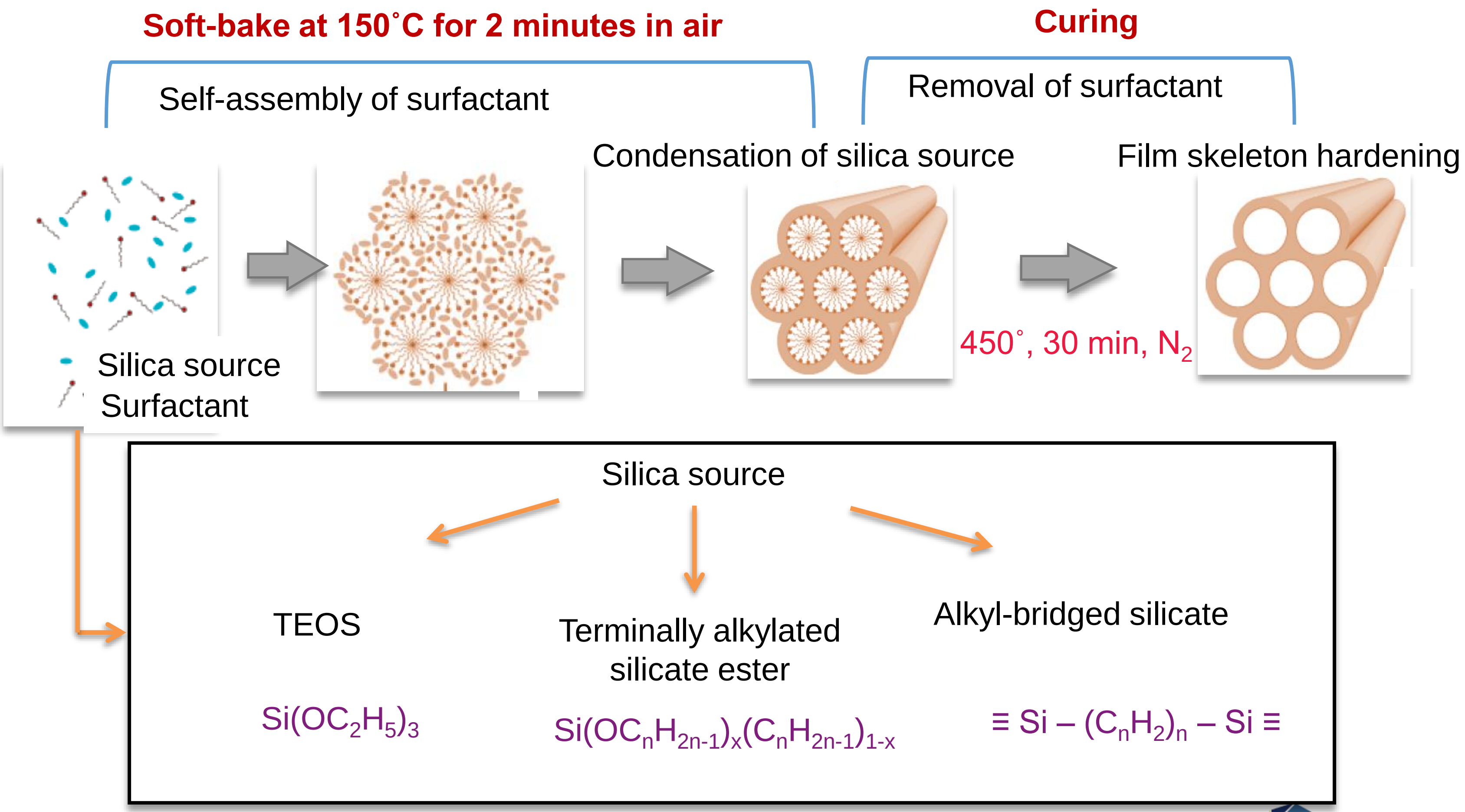
- PAS and EP are only 2 techniques suitable for evaluation of thin films when the amount of materials is not sufficient for classical nitrogen porosimetry. This is the reason why both these techniques are used in nanoelectronics for evaluation of thin porous films.

- These techniques are based on completely different physical ideas. PAS measures reduction of Ps lifetime when they collide with pore wall, EP measures radius of curvature of a liquid condensed in the pores.

- This is the reason why cross evaluation of the obtained results is very important.

Experiment - Samples

Periodic mesoporous organosilicates (PMO)- based low-k



Soft-bake at 150˚C for 2 minutes in air

Curing

Self-assembly of surfactant

Removal of surfactant

Condensation of silica source

Film skeleton hardening

Silica source

Surfactant

450°, 30 min, N_2

Silica source

TEOS

$Si(OC_2H_5)_3$

Terminally alkylated silicate ester

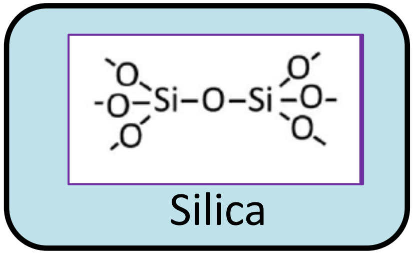
$Si(OC_nH_{2n-1})_x(C_nH_{2n-1})_{1-x}$

Alkyl-bridged silicate

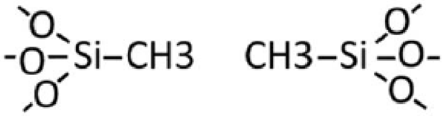
$\equiv Si - (C_nH_2)_n - Si \equiv$

Experiment - Samples

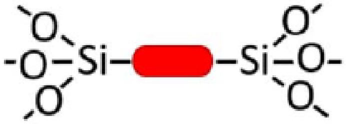
The matrix composition was changed from pure methyl terminated (MTMS) to fully benzene bridged material



MTMS*/BTESB** mol ratio	Porogen conc. (Brij L4) Wt.%
100/0	0
100/0	30
75/25	30
55/45	30
40/60	30
0/100	30
0/100	0



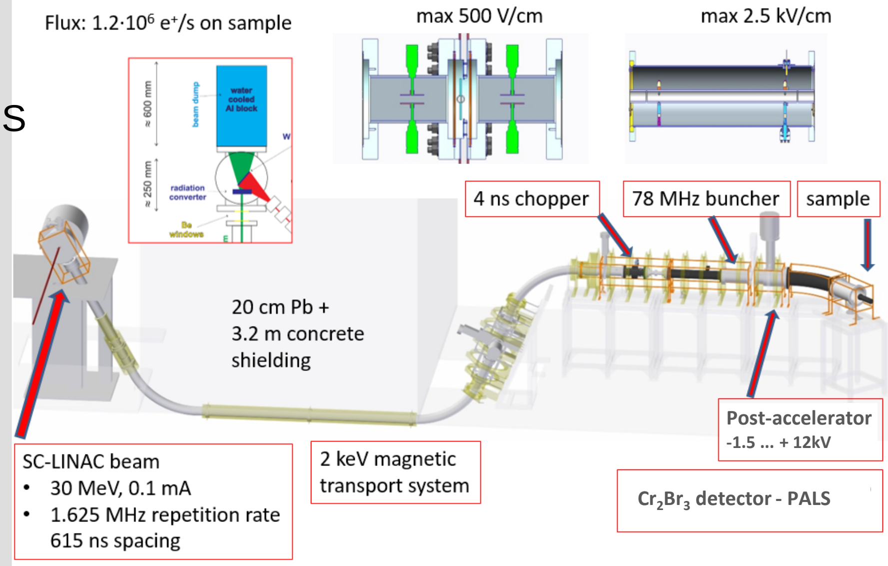
*MTMS – Methyltrimethoxysilane: Methyl terminated



** BTESB - 1,4-bis(triethoxysilyl)-benzene: Benzene bridged

Experiment - PAS

MePS



Flux: $1.2 \cdot 10^6$ e^+/s on sample

max 500 V/cm

max 2.5 kV/cm

4 ns chopper

78 MHz buncher

sample

20 cm Pb +
3.2 m concrete
shielding

Post-accelerator
-1.5 … + 12kV

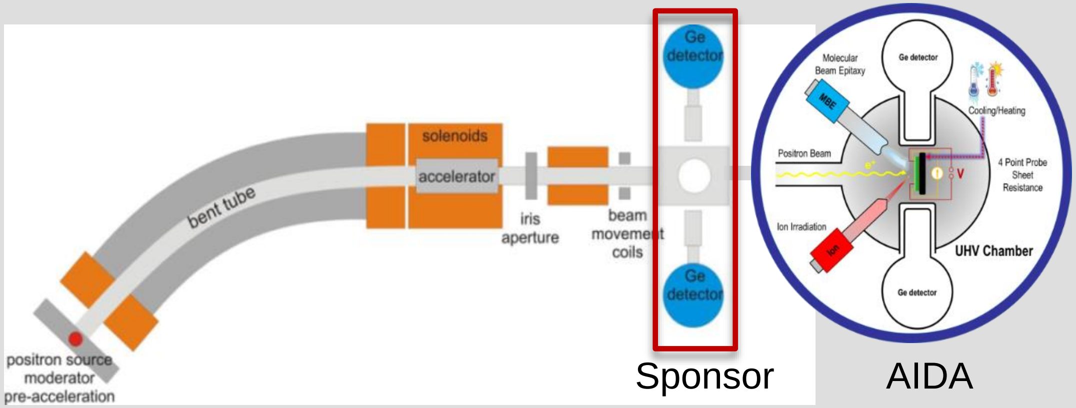
SC-LINAC beam
- 30 MeV, 0.1 mA
- 1.625 MHz repetition rate
  615 ns spacing

2 keV magnetic
transport system

Cr_2Br_3 detector - PALS

PALS

- thin films (500 eV – 12 keV)
- annihilation lifetime
- defects and porosimetry
- in situ annealing to purge pores



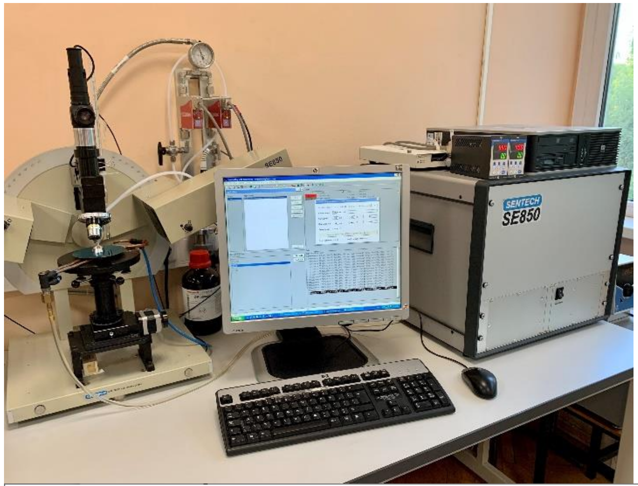
Sponsor

AIDA

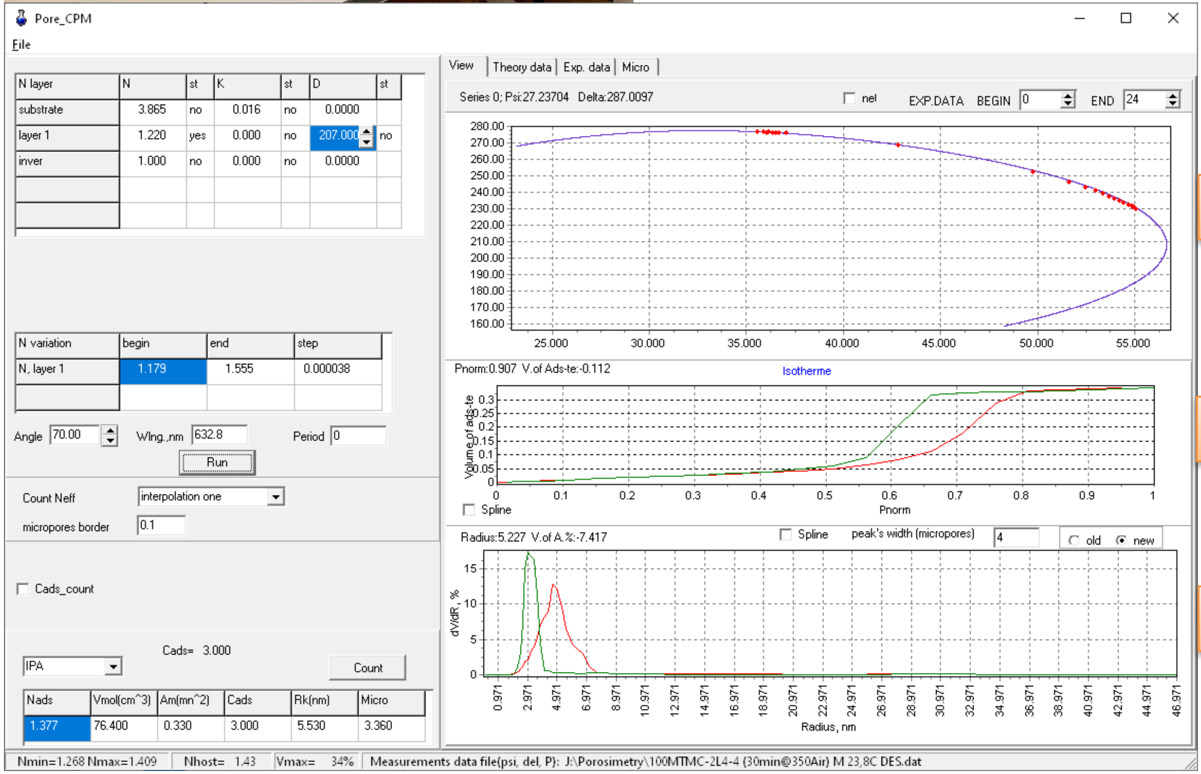
DB-PAS

- ^{22}Na-based e^+ source
- Thin films (30 eV – 35 keV)
- Doppler broadening + cDB
- in situ heating (AIDA)

Experiment - EP



- Porosity and Pore size distribution
- Young Modulus
- Barrier integrity
- Sealing & Modification
- Plasma damage
- Swelling



N layer	N	st	K	st	D	st
substrate	3.865	no	0.016	no	0.0000	
layer 1	1.220	yes	0.000	no	207.000	no
inver	1.000	no	0.000	no	0.0000	

N variation	begin	end	step
N, layer 1	1.179	1.555	0.000038

Angle 70.00 Wlng.,nm 632.8 Period 0

Count Neff: interpolation one

micropores border: 0.1

☐ Cads_count

IPA

Cads= 3.000

Nads	Vmol(cm^3)	Am(mn^2)	Cads	Rk(nm)	Micro
1.377	76.400	0.330	3.000	5.530	3.360

Series 0; Psi:27.23704 Delta:287.0097 ☐ nel EXP.DATA BEGIN 0 END 24

Pnorm:0.907 V.of Ads-te:-0.112

☐ Spline

Radius:5.227 V.of A.%:-7.417 ☐ Spline peak's width (micropores) 4 ○ old ● new

Nmin=1.268 Nmax=1.409 | Nhost= 1.43 | Vmax= 34% | Measurements data file(psi, del, P): J:\Porosimetry\100MTMC-2L4-4 (30min@350Air) M 23,8C DES.dat

Delta/Psi fitting

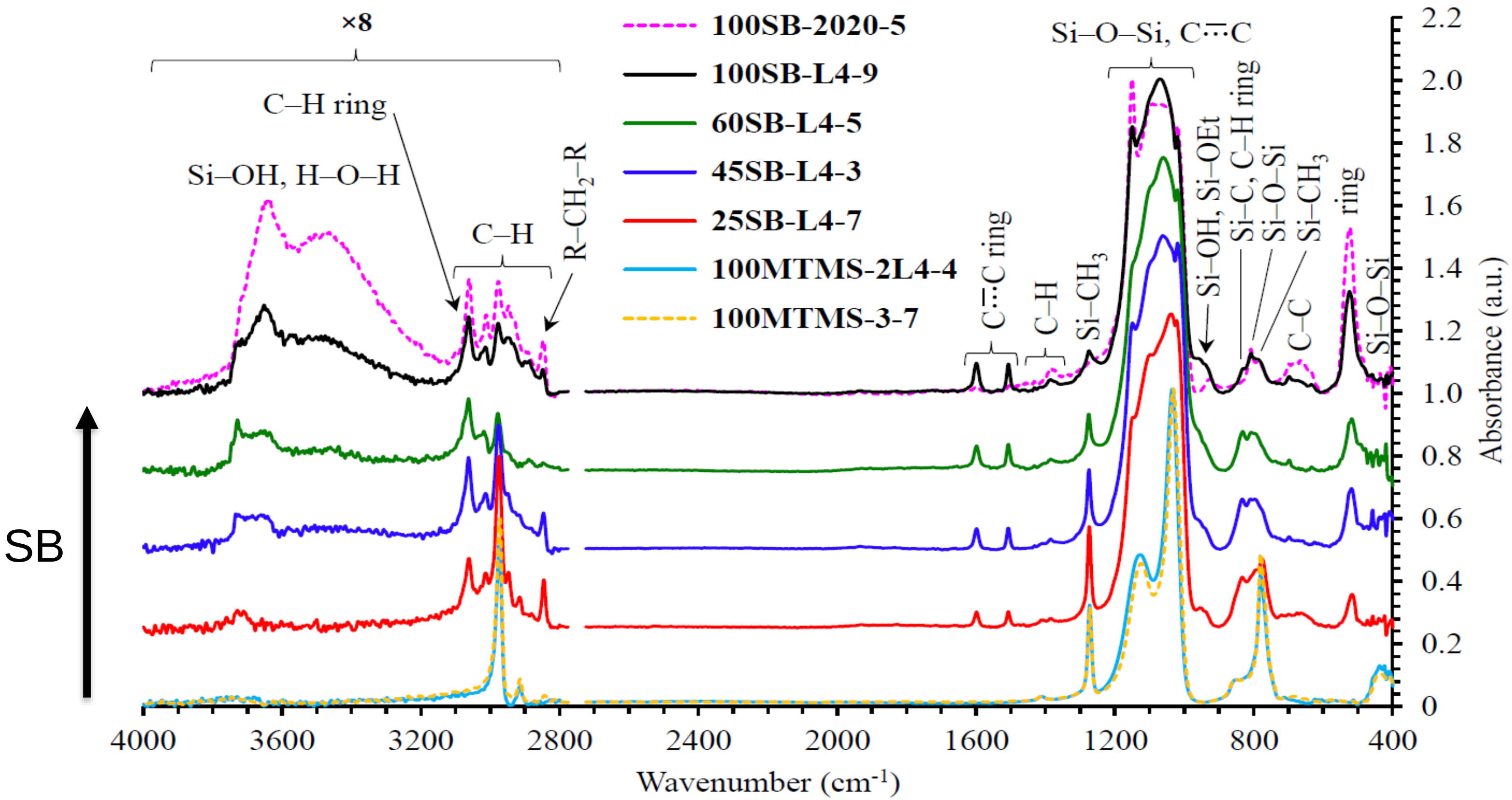
Adsorption isotherms

Pore size distribution

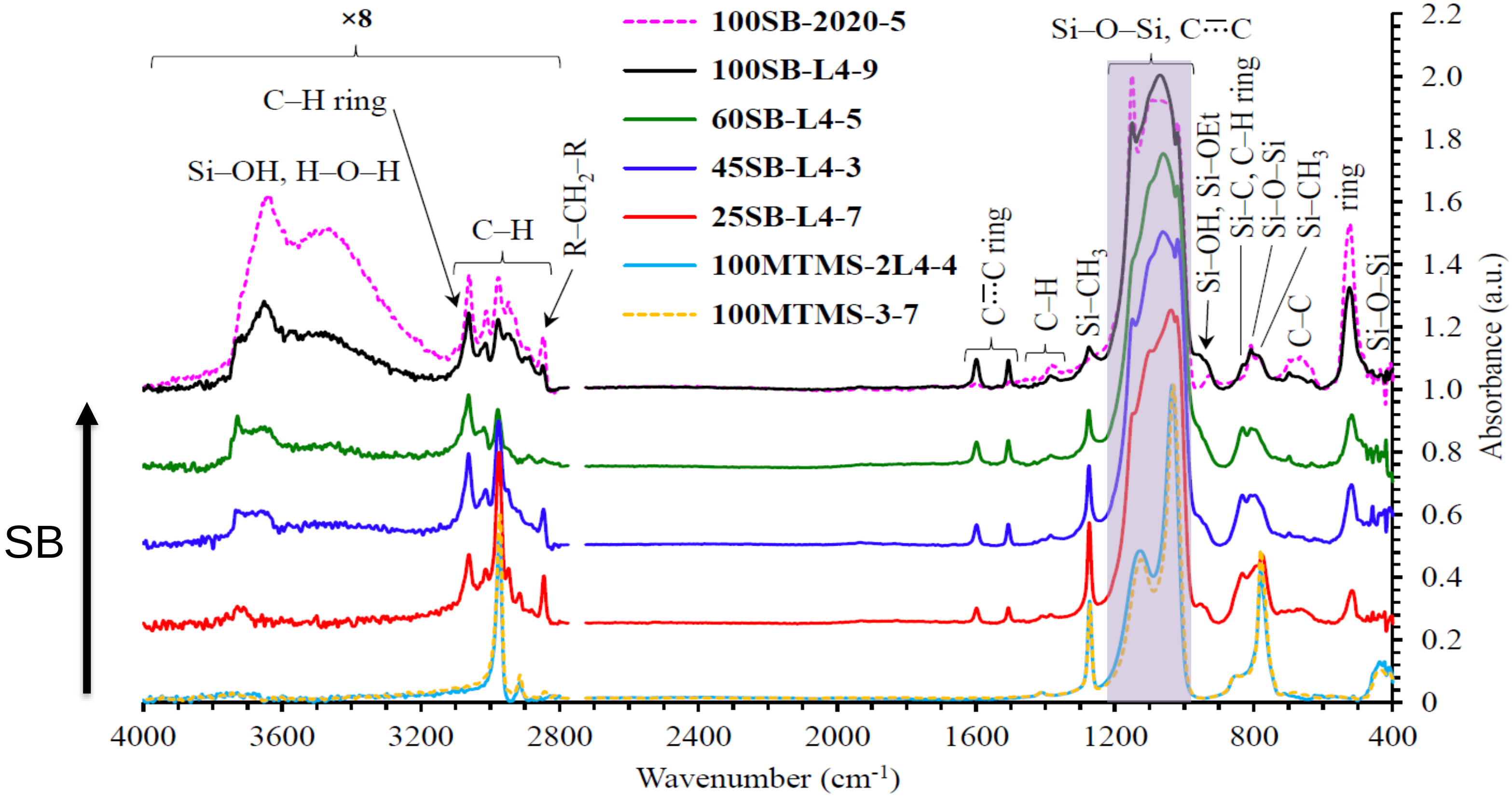
DRESDEN concept

HZDR

Results – Chemical comoposition (FTIR)

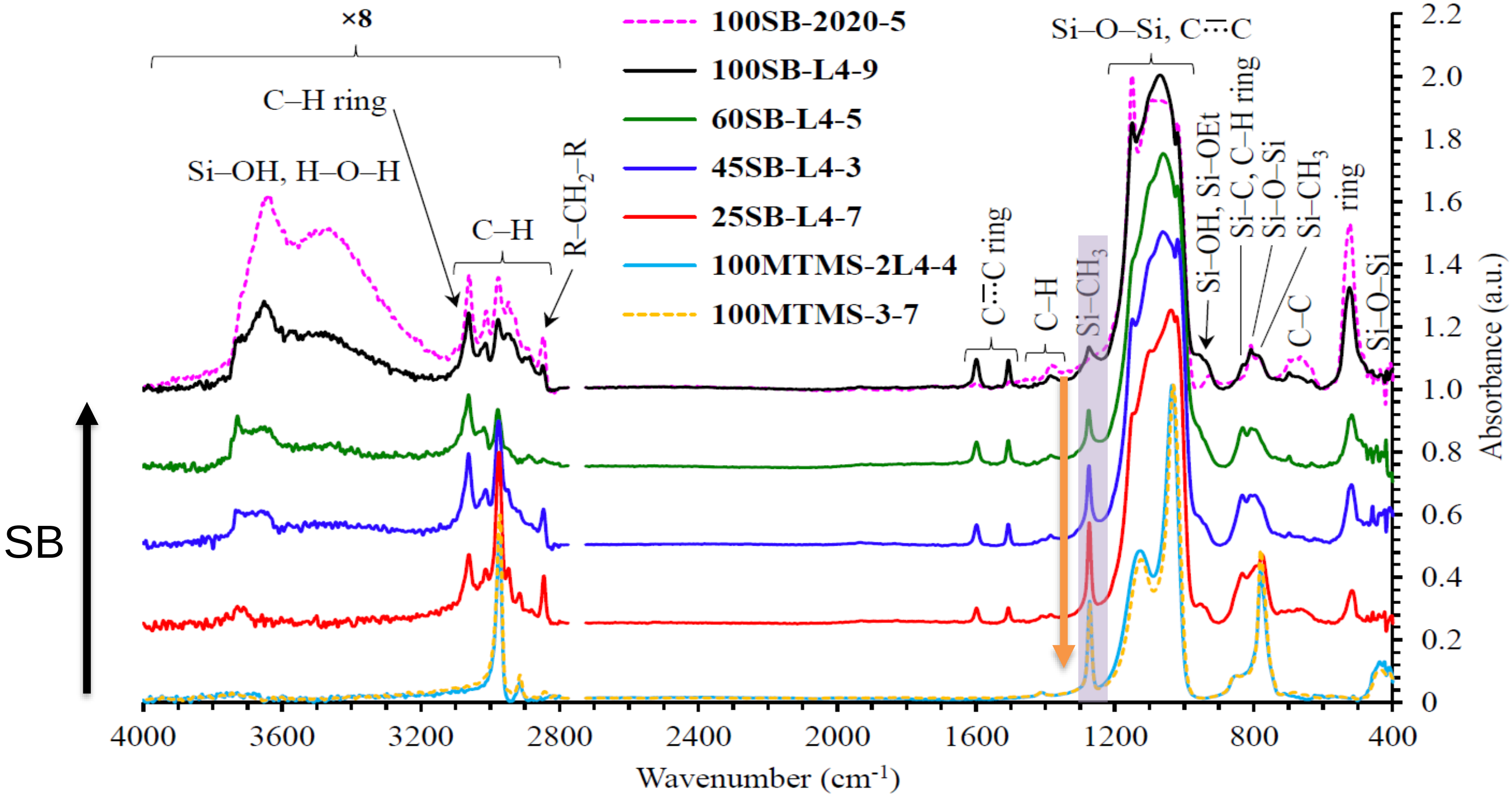


Results – Chemical composition (FTIR)



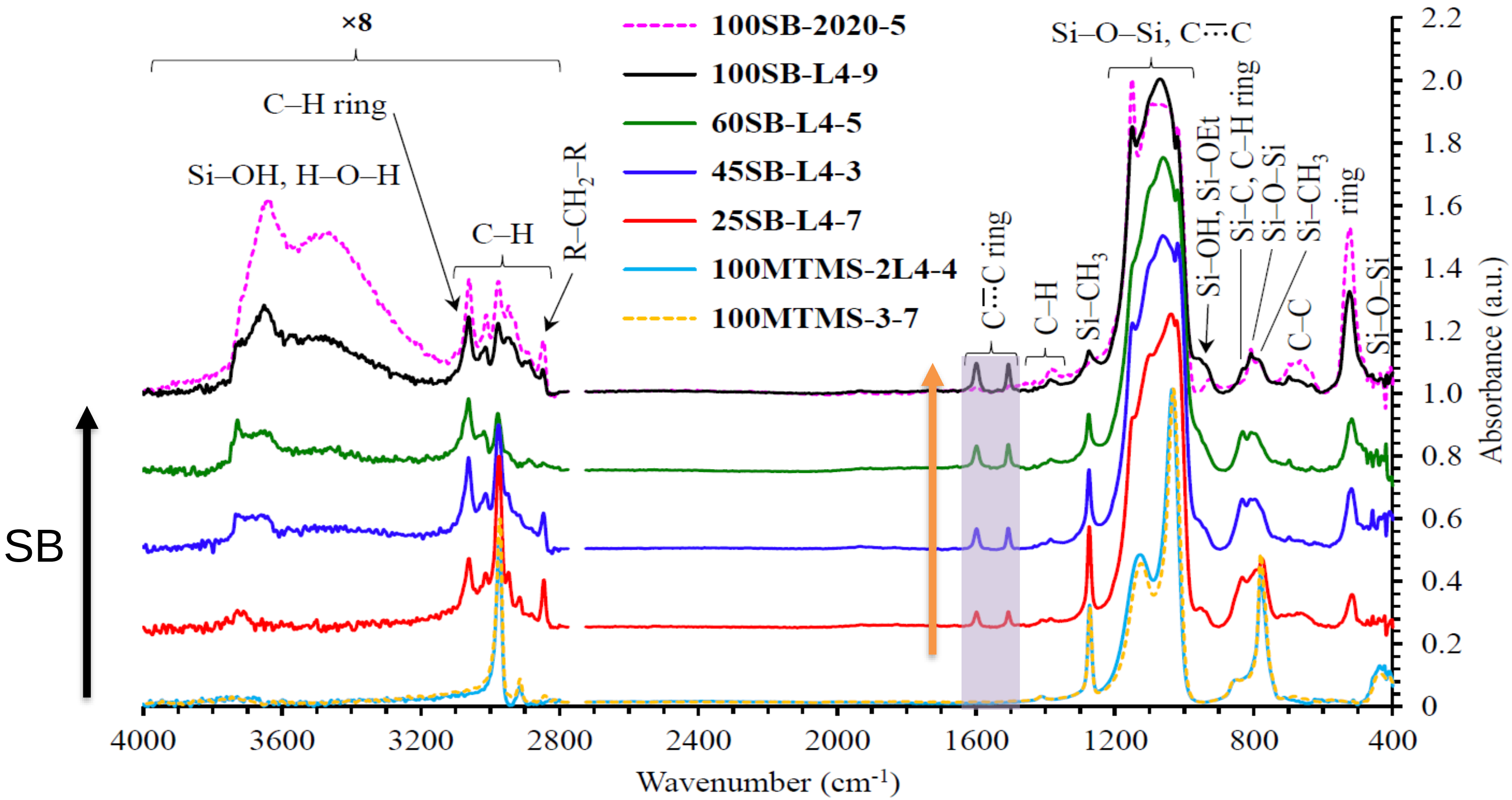
- Intensive peak at 1000-1100 cm^{-1} suggests formation of Silica like skeleton

Results – Chemical composition (FTIR)



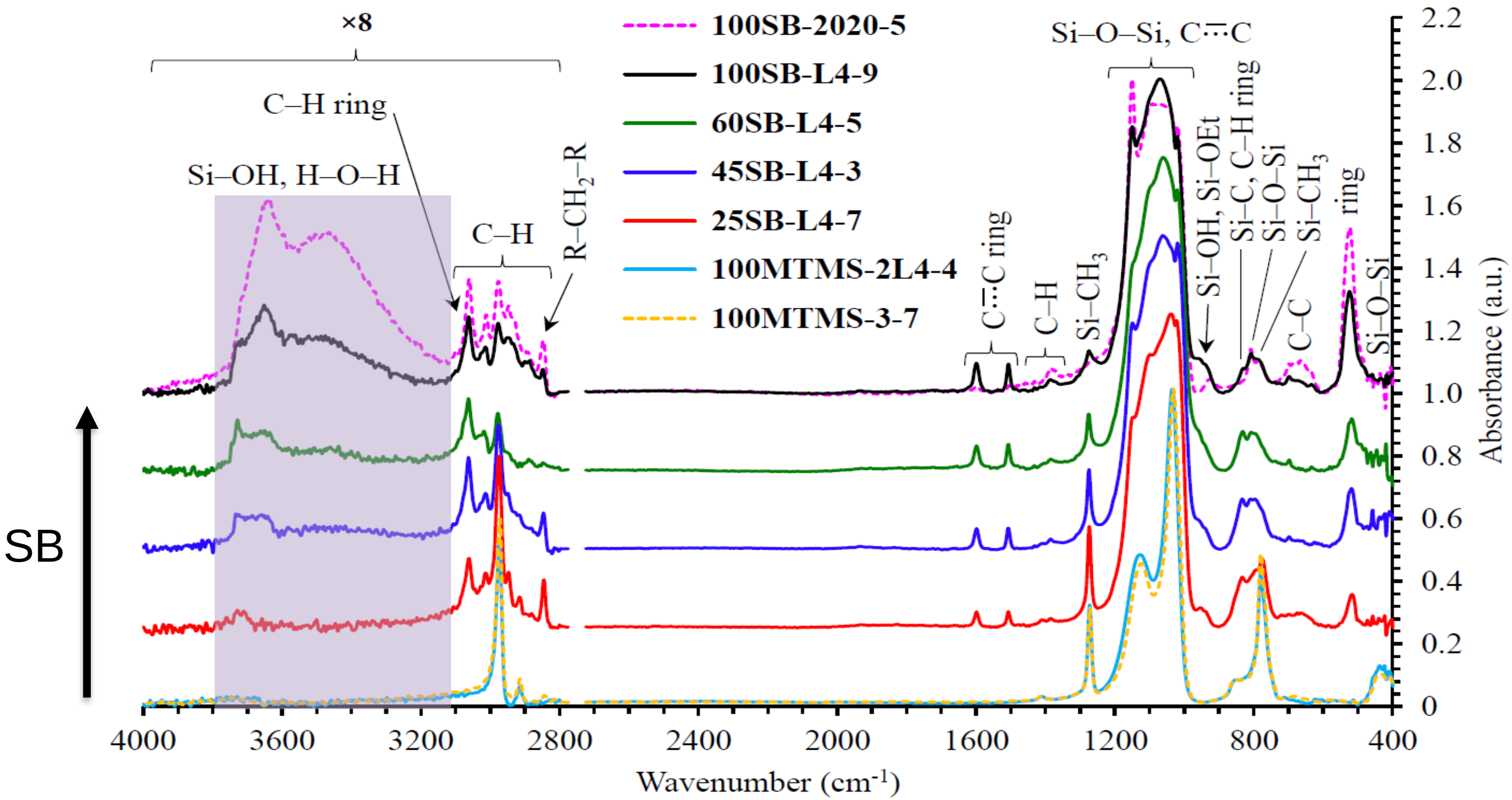
- Intensive peak at 1000-1100 cm^{-1} suggests formation of Silica like skeleton
- The peak at 1275 cm^{-1} shows concentration of -CH_3 terminals (max in MTMS film)

Results – Chemical composition (FTIR)



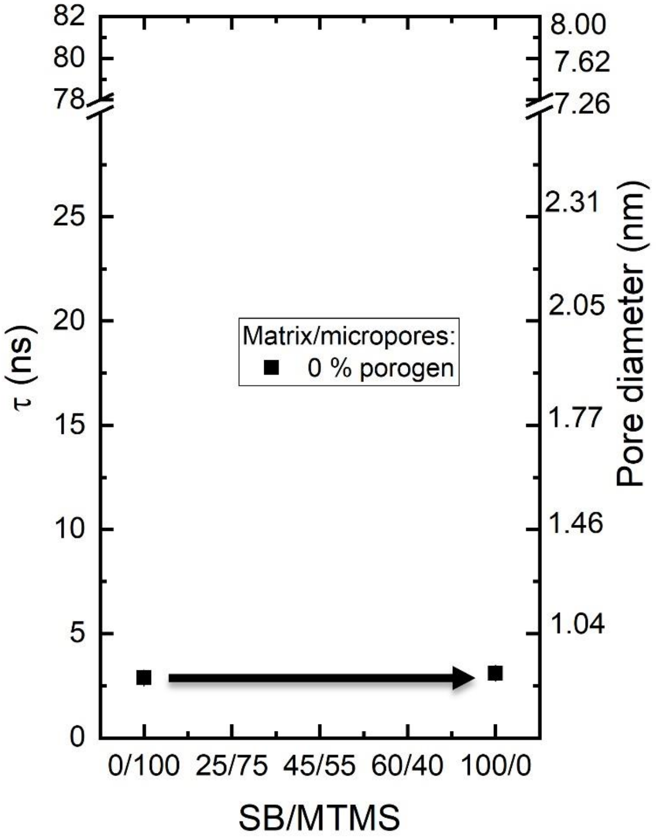
- Intensive peak at 1000-1100 cm^{-1} suggests formation of Silica like skeleton
- The peak at 1275 cm^{-1} shows concentration of -CH$_3$ terminals (max in MTMS film)
- Two peaks at 1500-1600 cm^{-1} are related to benzene bridge. (max in BTESB film)

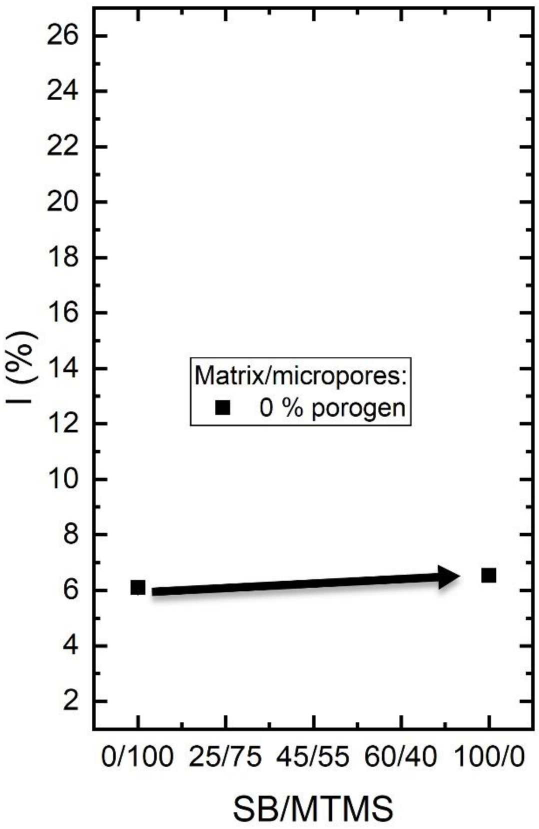
Results – Chemical composition (FTIR)



- ➢ Intensive peak at 1000-1100 cm^{-1} suggests formation of Silica like skeleton
- ➢ The peak at 1275 cm^{-1} shows concentration of -CH_3 terminals (max in MTMS film)
- ➢ Two peaks at 1500-1600 cm^{-1} are related to benzene bridge. (max in BTESB film)
- ➢ Benzene bridged films are not hydrophobic (water peaks at 3100-3700 cm^{-1}). Therefore, the presence of methyl terminals are important.

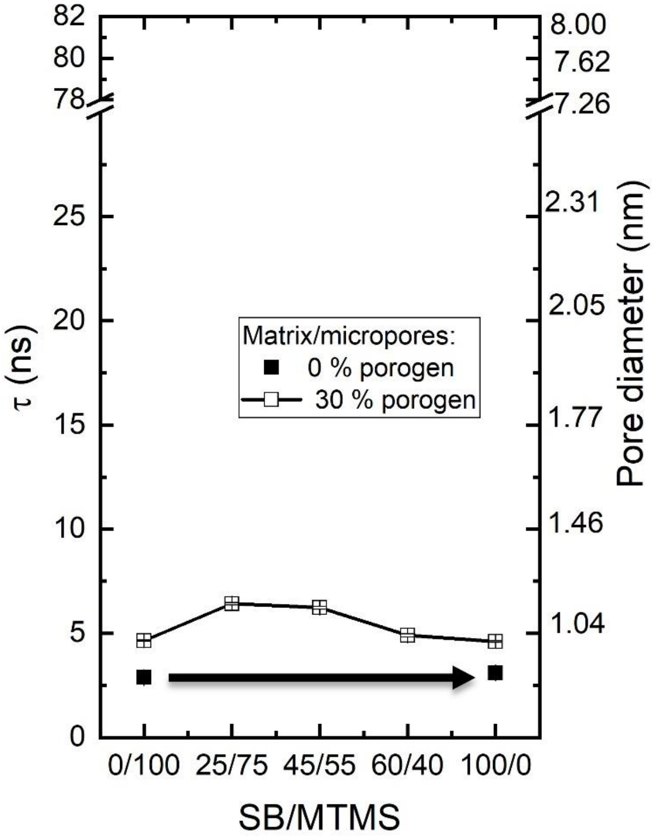
Results - PALS

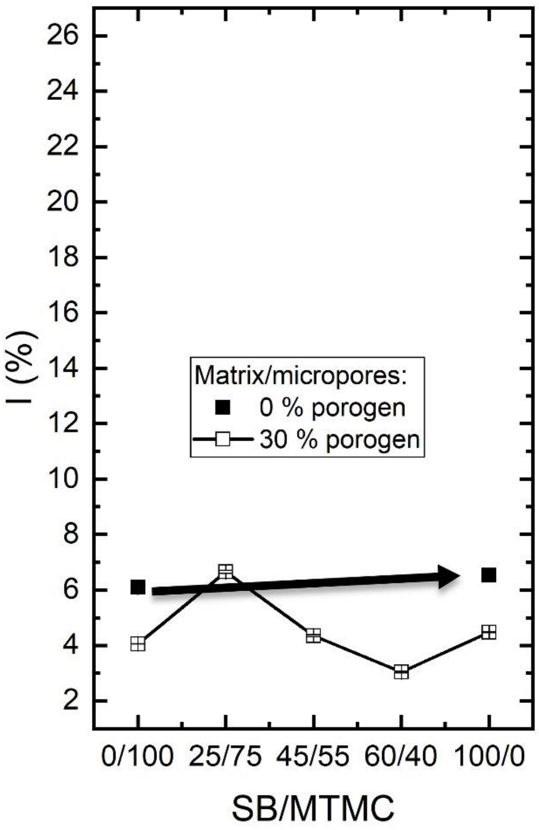




- o-Ps lifetime measures 0.77 nm matrix free volume in 100SB and 100MTMS samples
- both samples have ~ 6% o-Ps intensity in the matrix

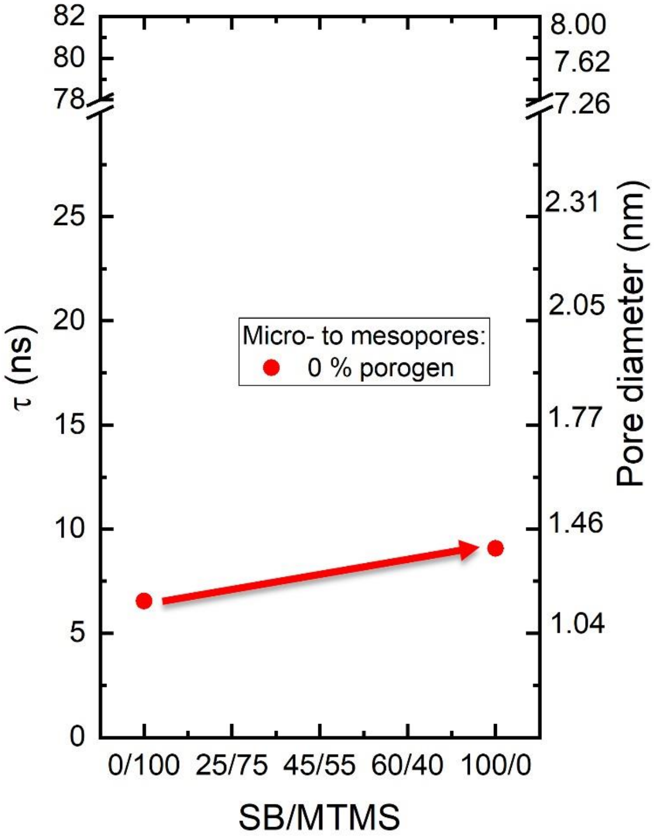
Results - PALS

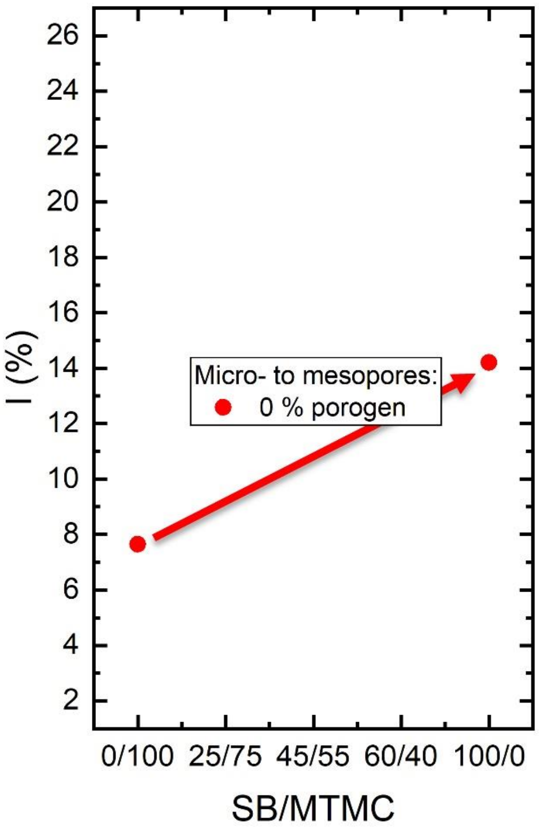




- o-Ps lifetime measures 0.77 nm matrix free volume in 100SB and 100MTMS samples
- both samples have ~ 6% o-Ps intensity in the matrix
- the matrix free volumes increased to ~ 1 nm when 30% porogen was added
- SB=25, 45% have the largest free volumes
- I_{matrix} mirrors the change of I_{meso} (see below)

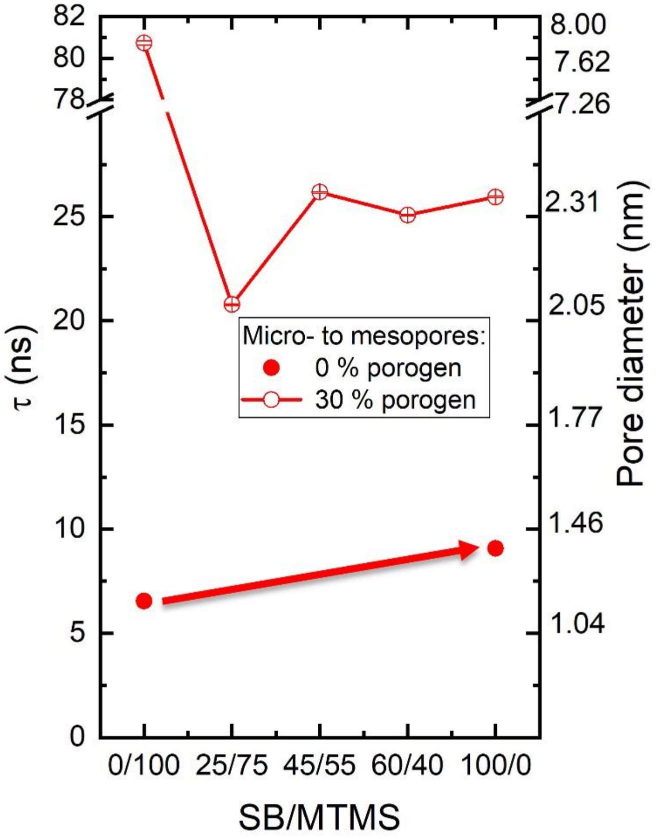
Results - PALS

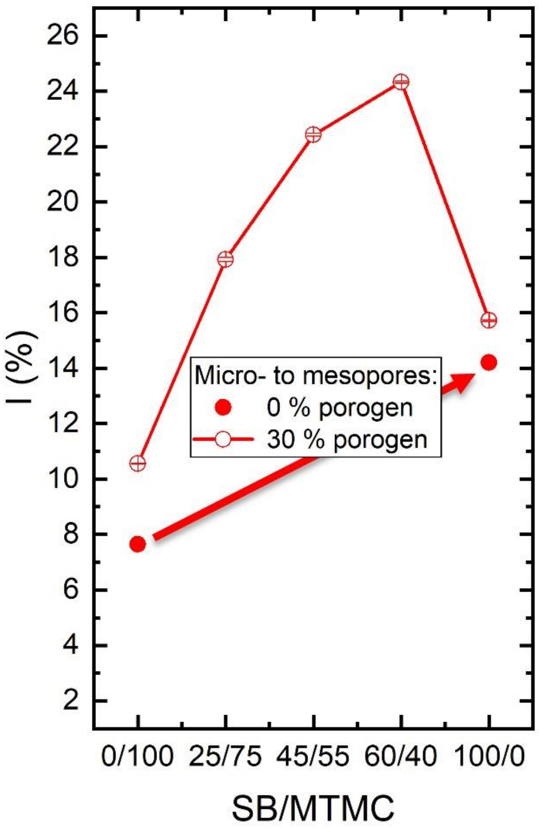




- 100SB and 100MTMS samples have micropores before adding porogen
- size and I of 100SB are higher

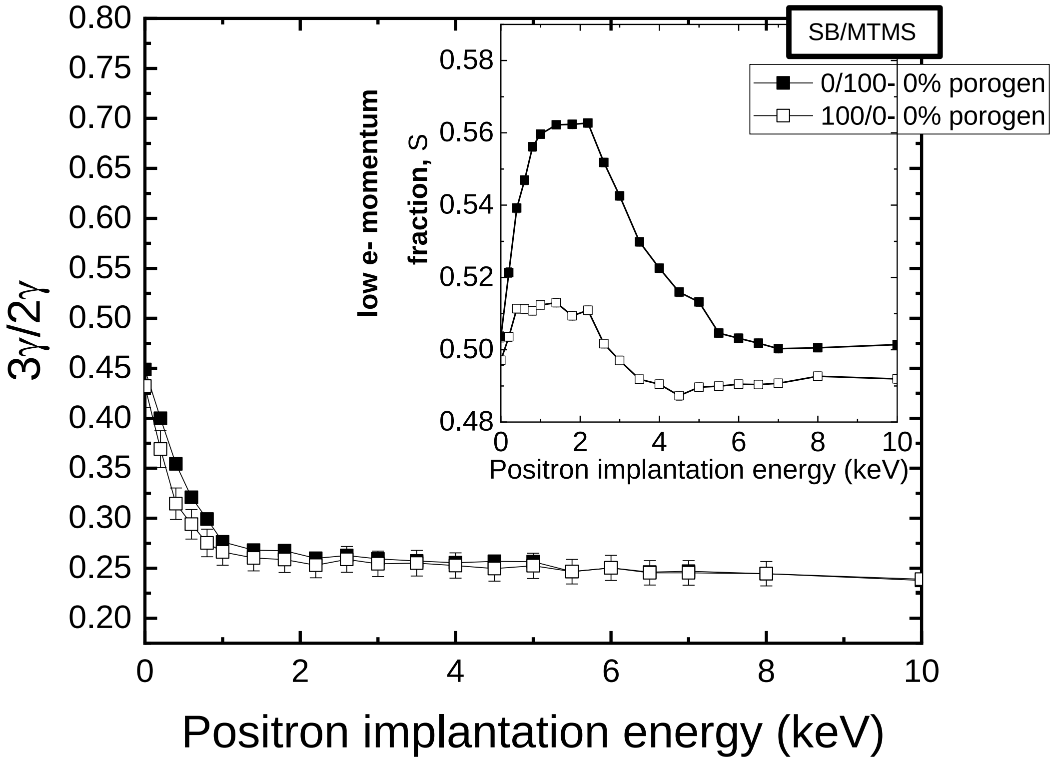
Results - PALS





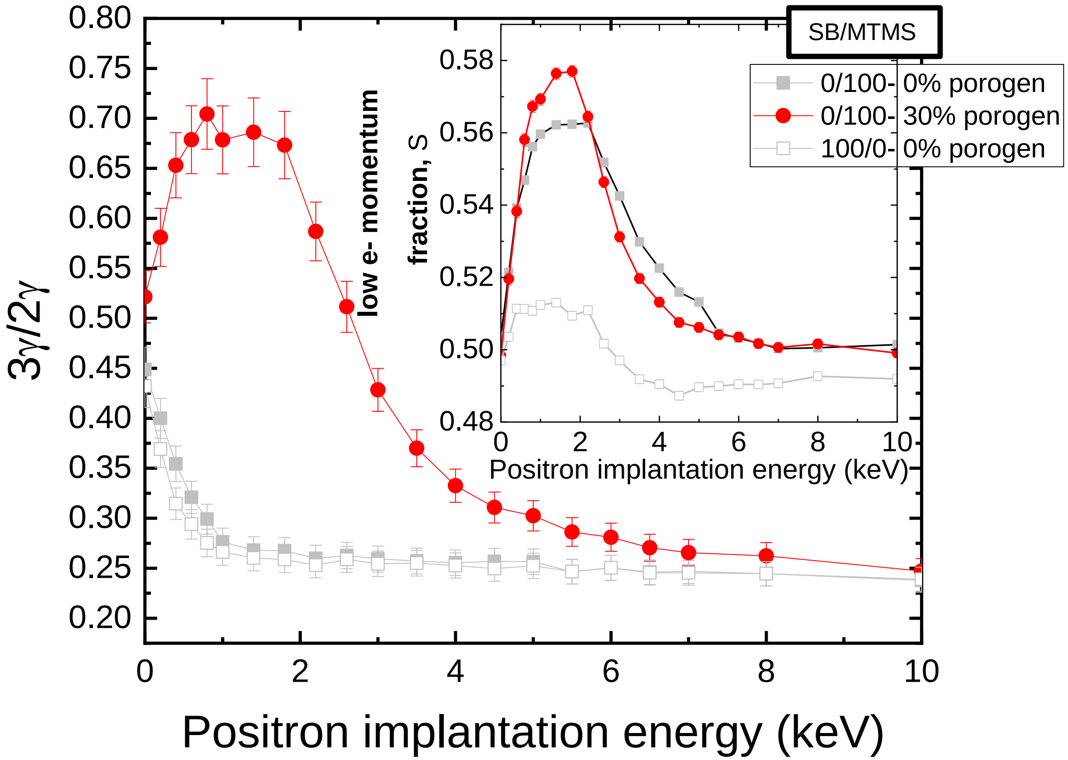
- 100SB and 100MTMS samples have micropores before adding porogen
- size and I of 100SB are higher
- mesopores are the largest in 100MTMS
- Transfor. of micro- to mesopores
- SB mesopores are smaller
- I_{meso} - 30% porogen ↑ → partial collaps of matrix to mesopores
- steep I_{meso} - SB-30% porogen
- 100SB-30% porogen → denser

Results – DB-PAS



- 3γ/2γ values → o-Ps escape (uncapped samples)
- Larger S.parameter in 100MTMC → higher pore+defect conc. ($I_2+I_3+I_4$)

Results – DB-PAS



- 3γ/2γ values → o-Ps escape (uncapped samples)
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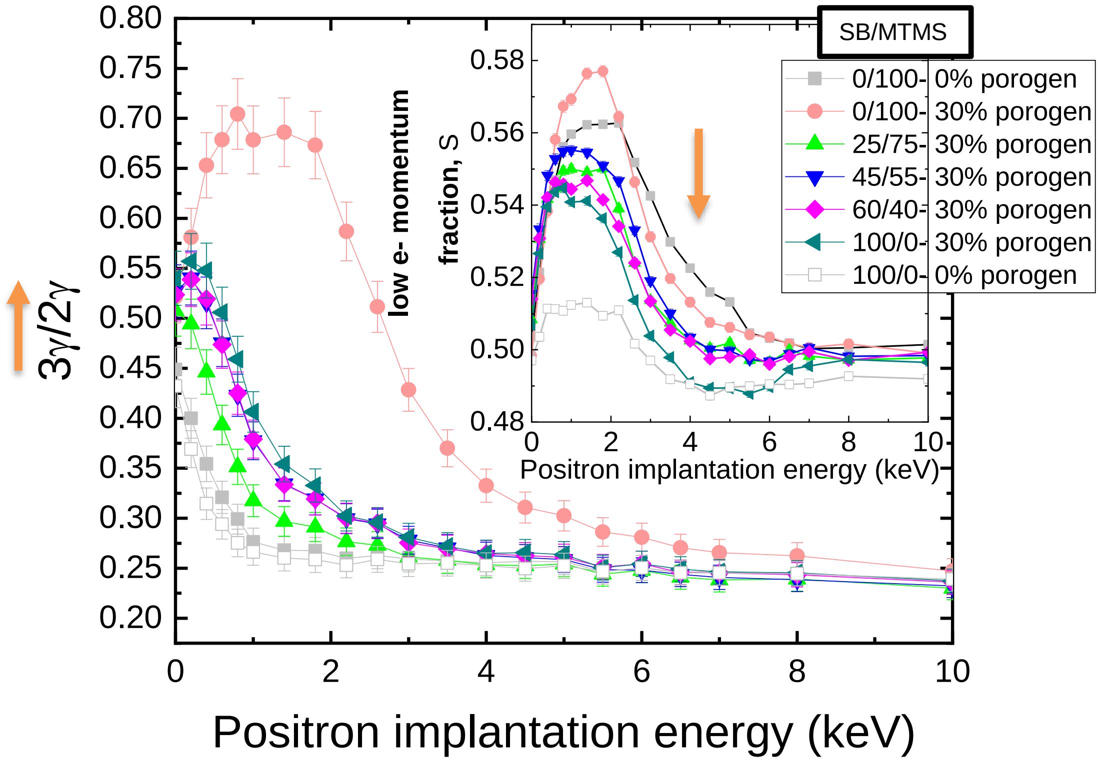
- Value and shape of 3γ/2γ in 100MTMS-30 % porogen → open and intercon. pores
- Large S-paramter→ big pores

Results – DB-PAS

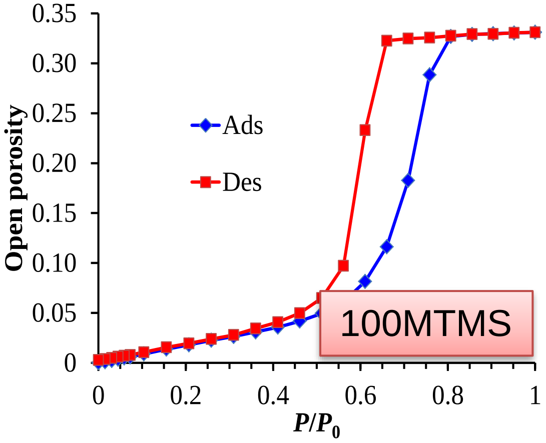


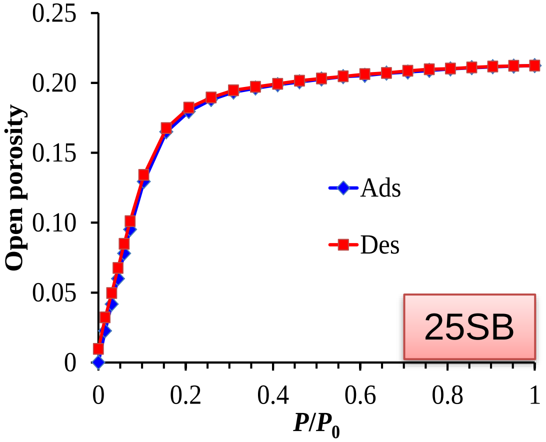
- 3γ/2γ values → o-Ps escape (uncapped samples)
- Larger S.parameter in 100MTMC → higher pore+defect conc. ($I_2+I_3+I_4$)
- Value and shape of 3γ/2γ in 100MTMS-30 % porogen → open and intercon. pores
- Large S-paramter→ big pores
- 3γ/2γ of SB<MTMS→ less intercon. and harder structure
- S-parameter drops with SB→ total defect conc. deceases with SB amount

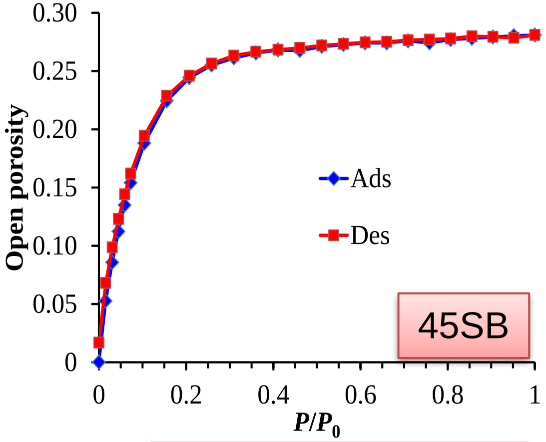
Results – EP – 30% porogen

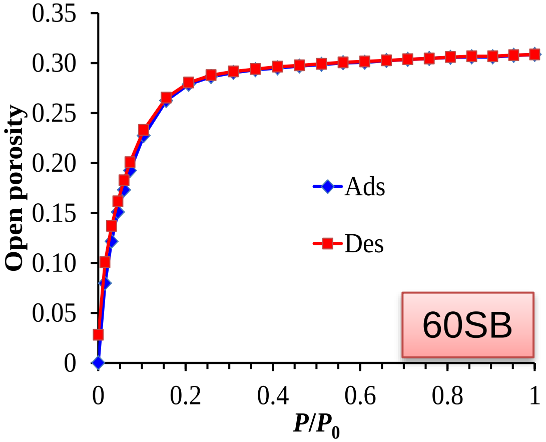
(the open porosity is varied in the range of 20-35%)

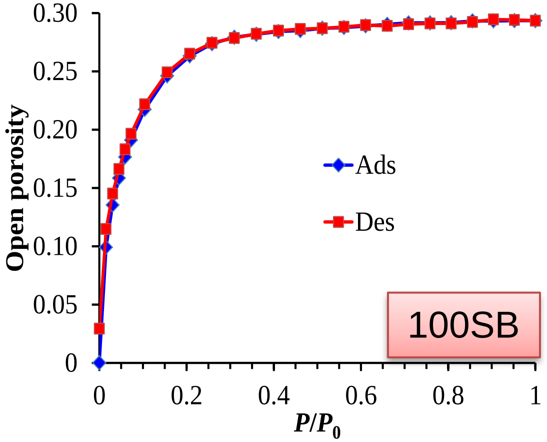
Isotherm

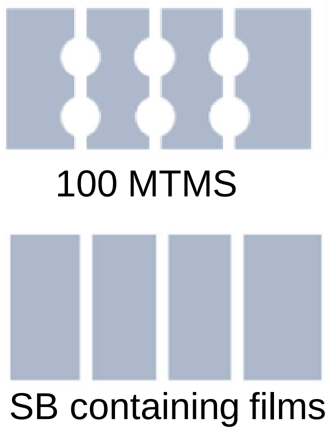








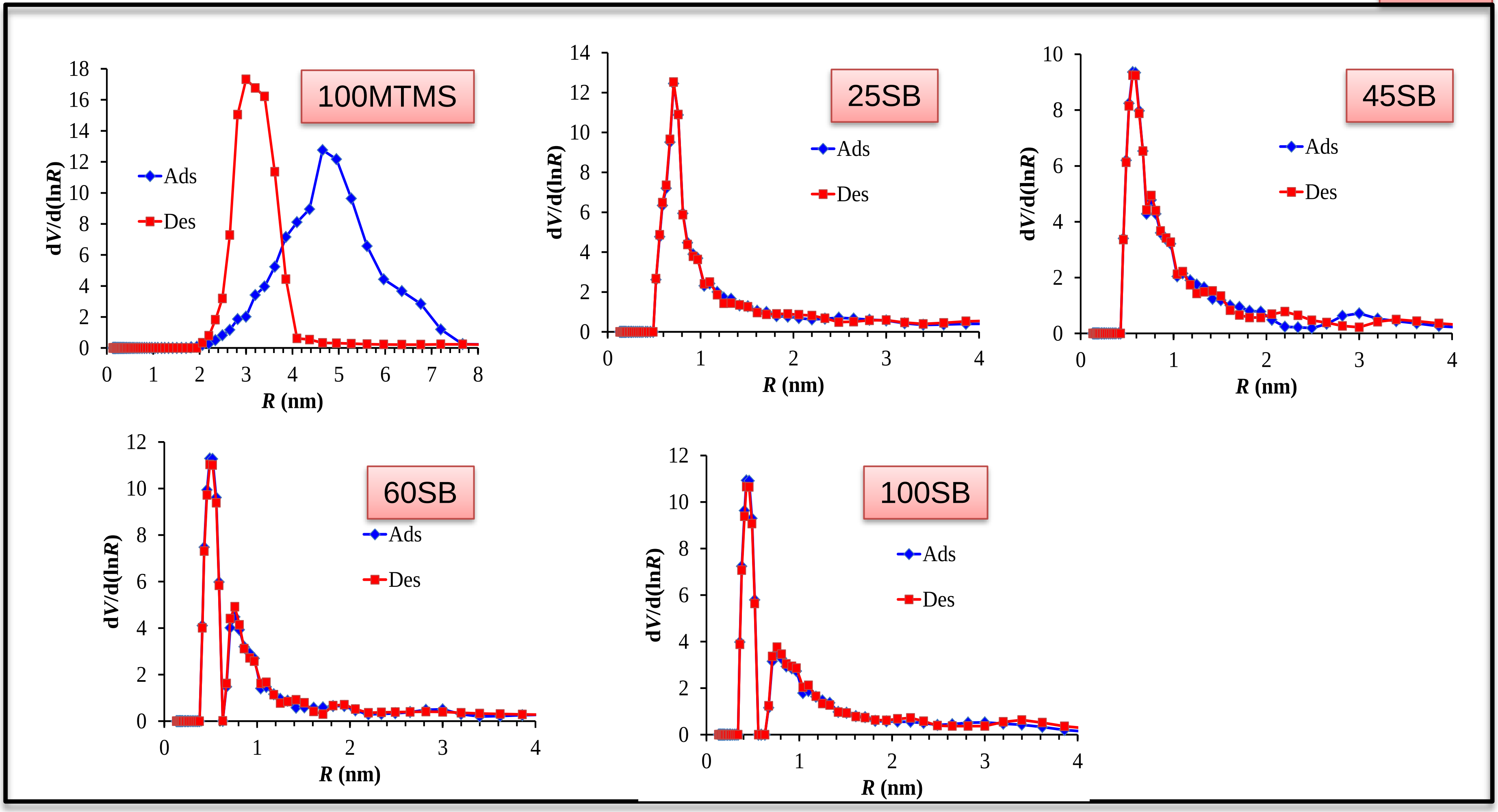




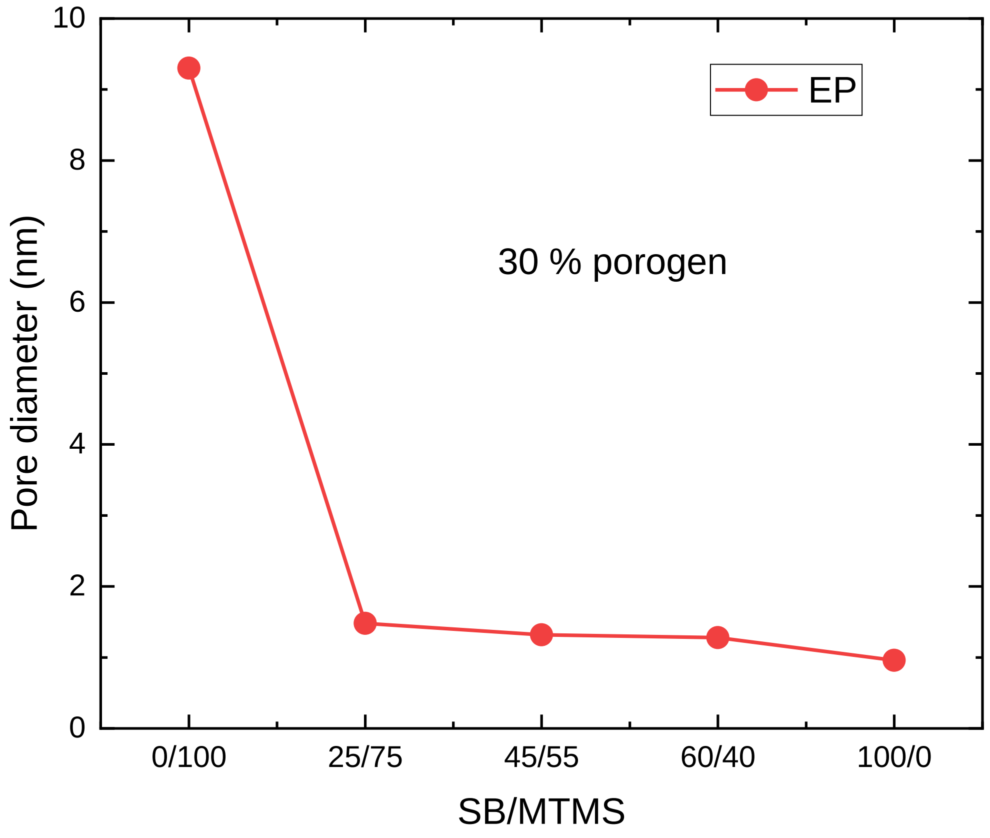
MTMS film has ink-bottle like shape, while other materials have cylindrical pores

Results – EP – 30% porogen

PSD

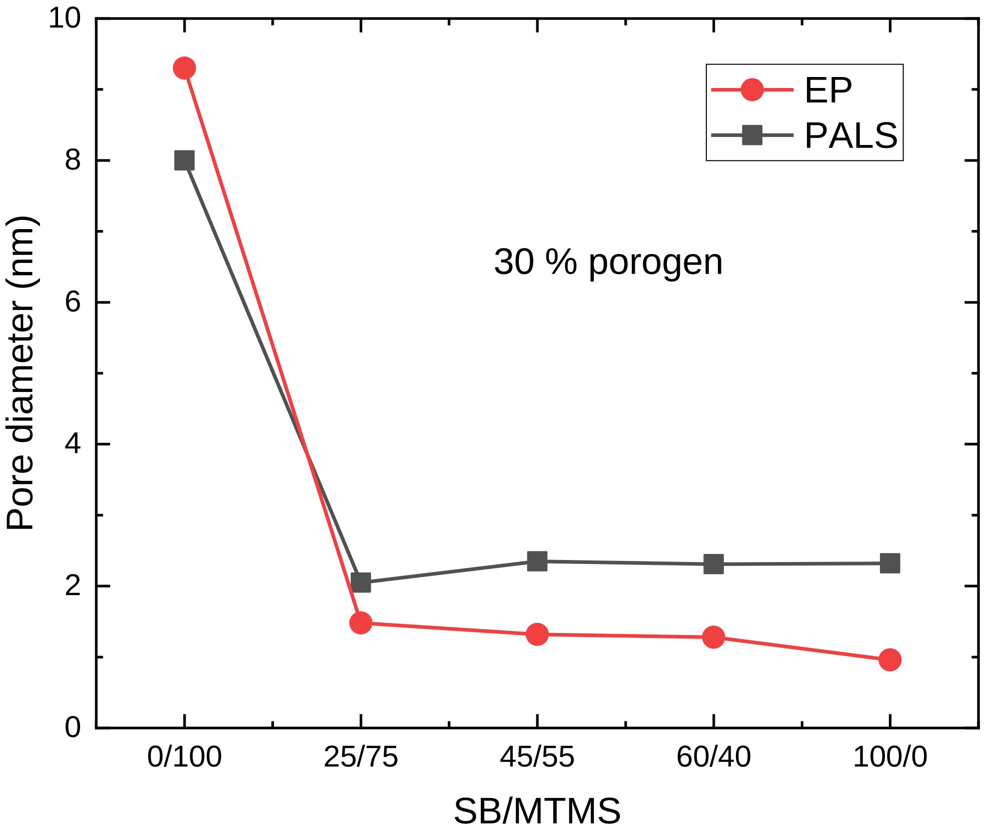


Results – EP – 30% porogen



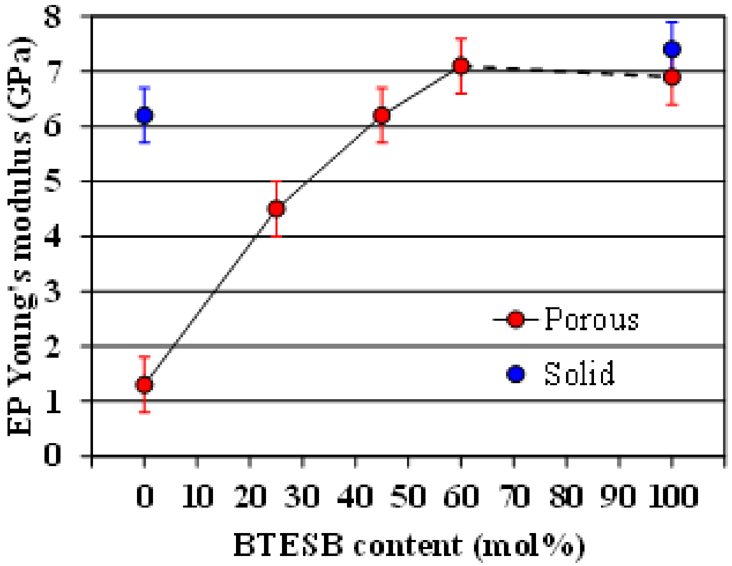
- Rapid drop in pore diameter is obtained when SB added
- Pore diameter slightly changes with increasing SB amount

Results – EP – 30% porogen



- Both methods show almost the same behavior

Results – EP – 30% porogen - YM



- From EP
- Nonporous materials (blue) have higher Young's modulus (E) than porous
- E increases with SB concentration
- E stabilizes after SB= 60%

Summary

- PAS and EP cross evaluation of low-k films with different composition gave good agreement. Small difference in the pore size can be related to sidewall roughness and presence of adsorbed impurities. They can change Ps lifetime (PAS) and impact to the meniscus formation in EP.

- Both techniques showed that pure methyl terminated films have larger pore size. Introduction of 25-75% of BTESB reduces pore size to the value typical for pure benzene bridged films.

- It is shown that benzene bridged films are more hydrophilic and contain adsorbed moisture. This result allows to conclude that presence of methyl terminals are needed although the benzene bridged films have better mechanical properties.

Thank you for your attention!

Backup

EP is adsorption porosimetry

It uses Lorenz-Lorentz equation (1) to calculate porosity and Kelvin equation (4) to calculate pore size.

$$\tan\Psi \exp(i\Delta) = \frac{R^p}{R^s} \Rightarrow n,\ d$$

$$B = \sum_i \frac{4\pi N_i}{3}\alpha_i = V\frac{n_1^2-1}{n_1^2+2} + (1-V)\frac{n_2^2-1}{n_2^2+2}$$

Full porosity: $V = 1 - \frac{B_p}{B_b} = 1 - \left[\frac{(n_p^2-1)}{n_p^2+2)}\right] \Big/ \left[\frac{(n_s^2-1)}{(n_s^2+2)}\right]$ (1)

Open pores: $V_{ads} = \frac{V_m}{\alpha_{ads} \cdot d_1}(B_1 d_1 - B_0 d_0)$ (2)

Pore interconnectivity: $x = V_{ads}/V$ (3)

Pore radius: $r = \frac{2\gamma V_L}{RT\ln(P/P_0)}$; $r = \frac{K}{4.574\sqrt{1/B}}$ (4)

Pore size distribution: $dV_{ads}/dr\ vs.\ r$ (5)

Specific surface area: $\delta A_i = 2\delta V_i / r_i;\ A = \sum \delta A_i^p\ (m^2/cm^3)$ (6)

B_s *is the volume of the film skeleton;* B_p *is the measured volume polarisability;*

V_m *is the molecular volume of the adsorptive,* α_{ads} *is the polarisability adsorptivemolecule;*

B_0 *and* d_0 *are the volume polarisability and thickness of the film before adsorption,*

B_1 *and* d_1 *are the volume polarisability and thickness of the film after adsorption*