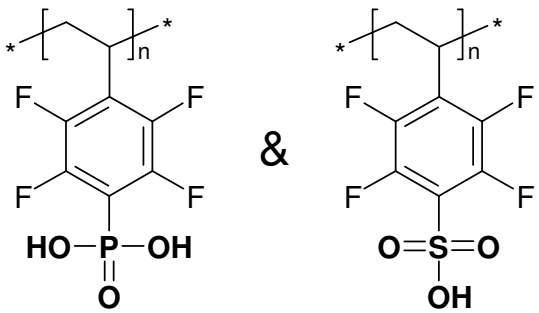
Phosphonated & sulfonated poly(pentafluorostyrene)

Vladimir Atanasov & Jochen Kerres

Institute of Chemical Process Engineering
University of Stuttgart, Germany



Outline

❖ Phosphonated poly(pentafluorostyrene) (PWN2010)

- Synthesis & Characterization
- Conductivity (EIS)
- Structure (SAXS)
- Anhydride formation (phosphonic acid condensation)
- Resistance to radical attack (Fentons test)

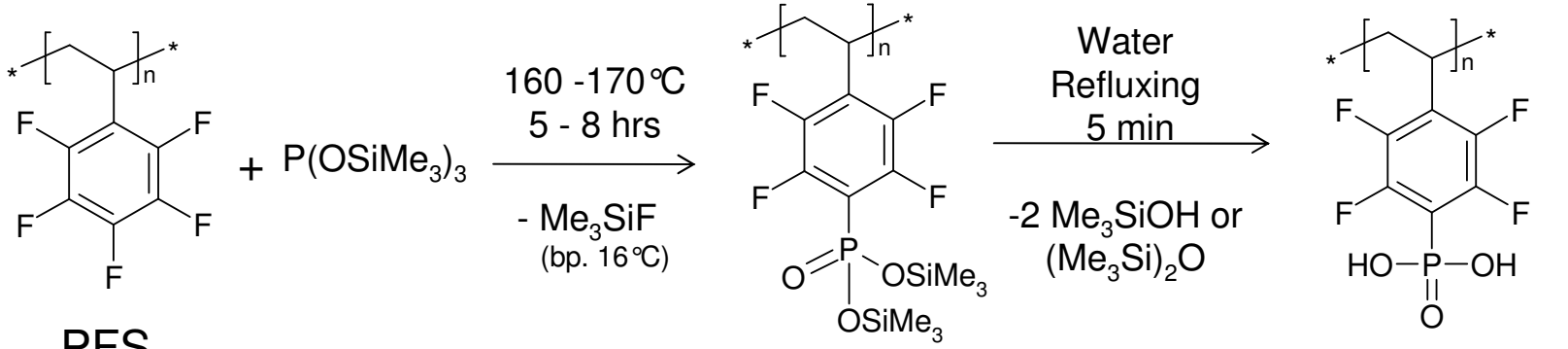
❖ Emulsion polymerization of pentafluorostyrene

- Molecular weight (GPC)

❖ Sulfonated poly(pentafluorostyrene) (sPFS)

- Synthesis & Characterization
- Resistance to heat (TGA)
- Hydration isotherms (water uptake)
- Conductivity (EIS)

Phosphonation of PFS



PFS
(commercial)

PWN2010

Characteristics:

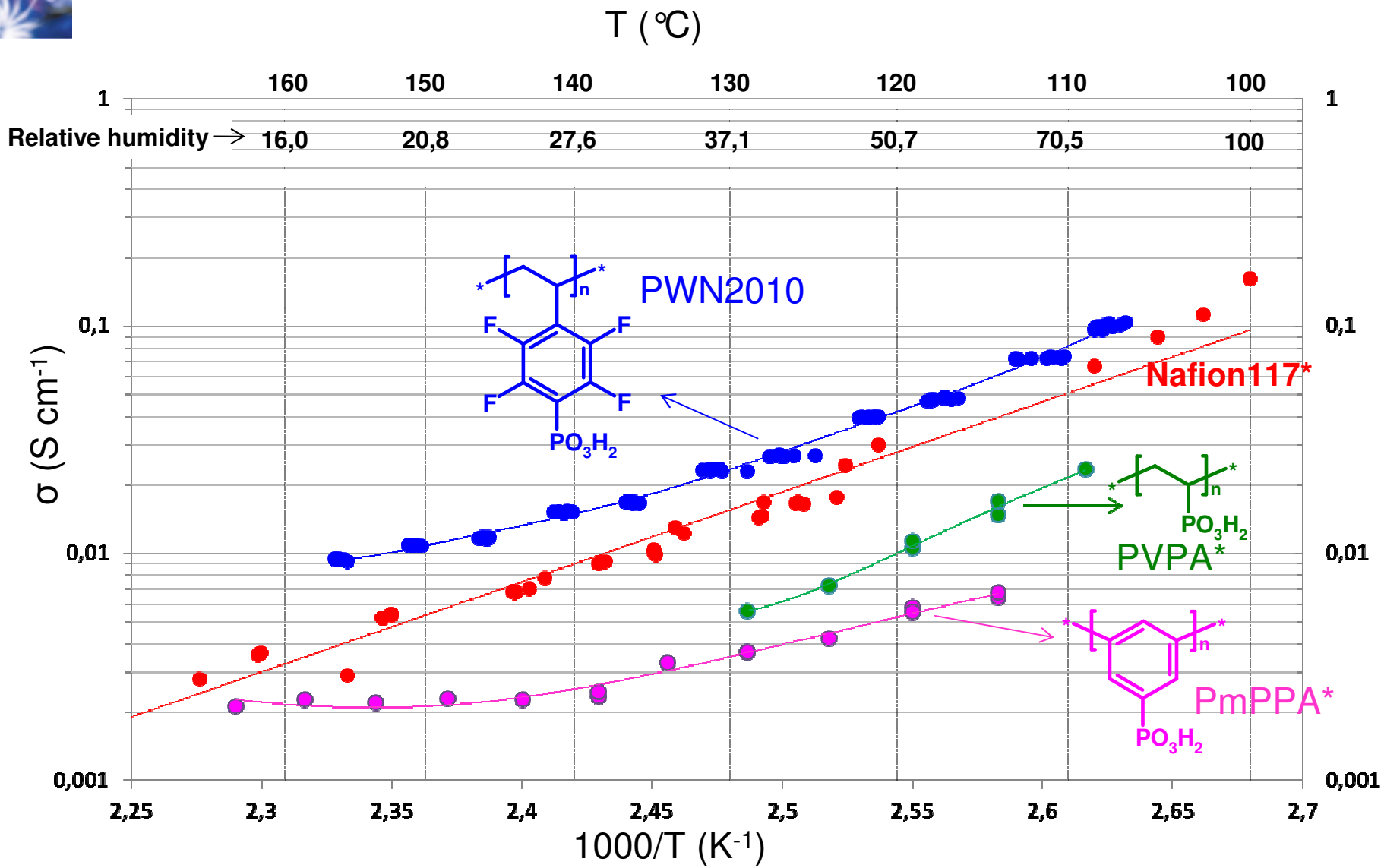
Yield: 98%

water soluble powder

- phosphonation above **90 %**
- molecular weight M_w = **67 kDa** (M_w (PFS) = 59 kDa)
- IEC = **7 mmol g^{-1}** (calc. 7.8 mmol g^{-1})
- pK_a^1 = **0.5** (Polystyrene-PO_3H_2: pK_a^1 = 1.9)
- resistance to heat up to **340 °C**
- T_g above **340 °C**

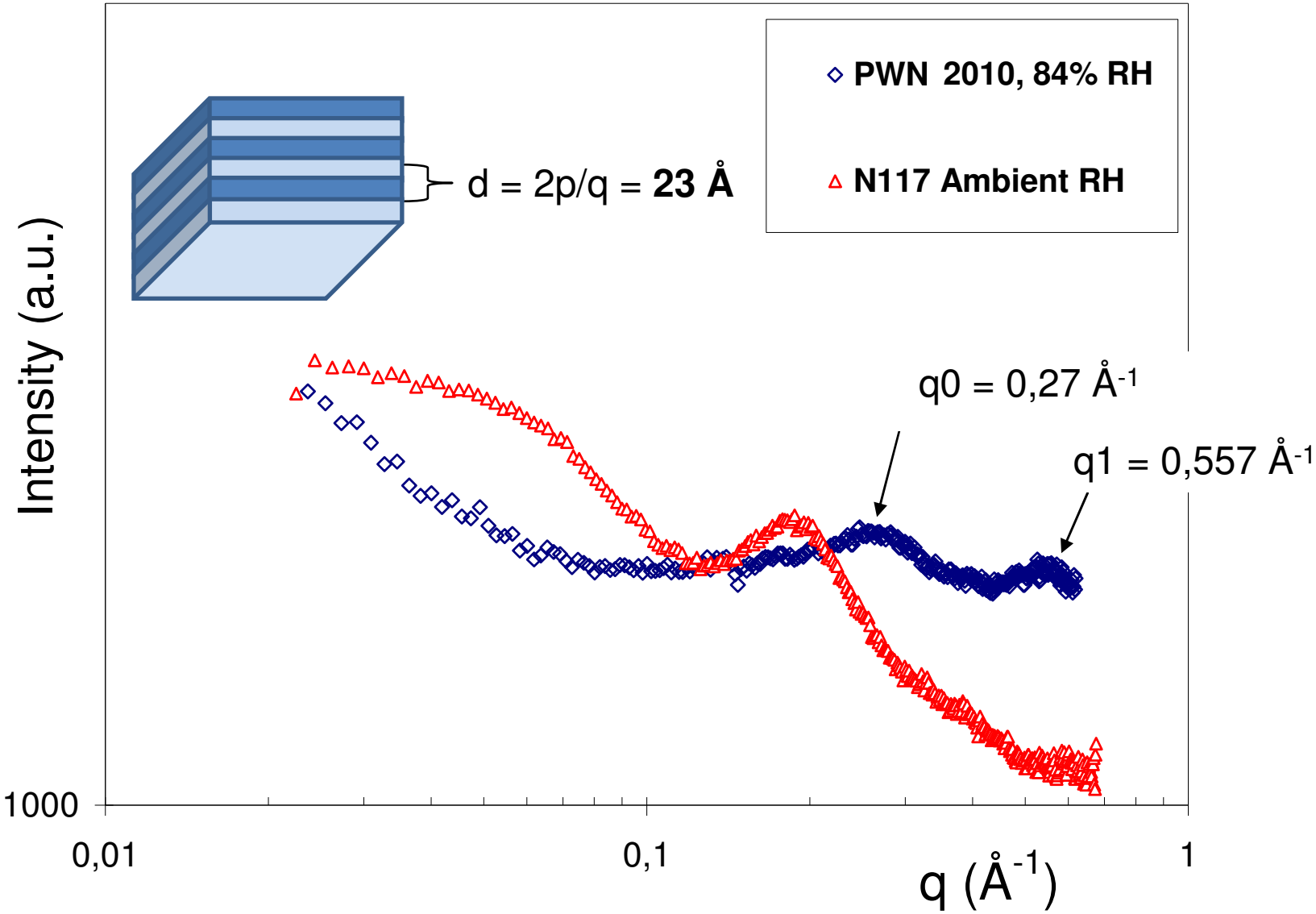
Atanasov & Kerres *Macromolecules* **2011**, 44, 6416

Conductivity at 1atm water pressure

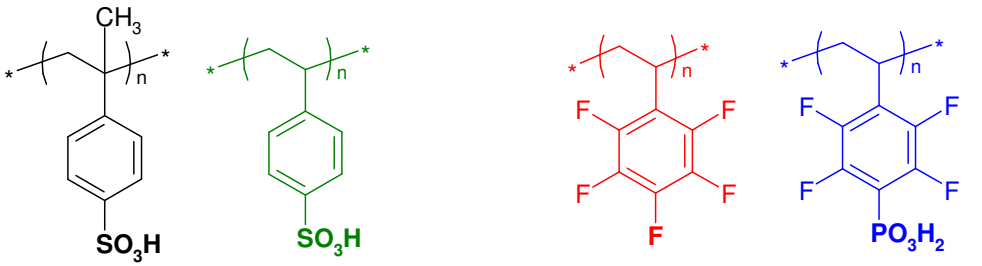


* H. Steininger *Phys. Chem. Chem. Phys.*, **2007**, 9, 1764

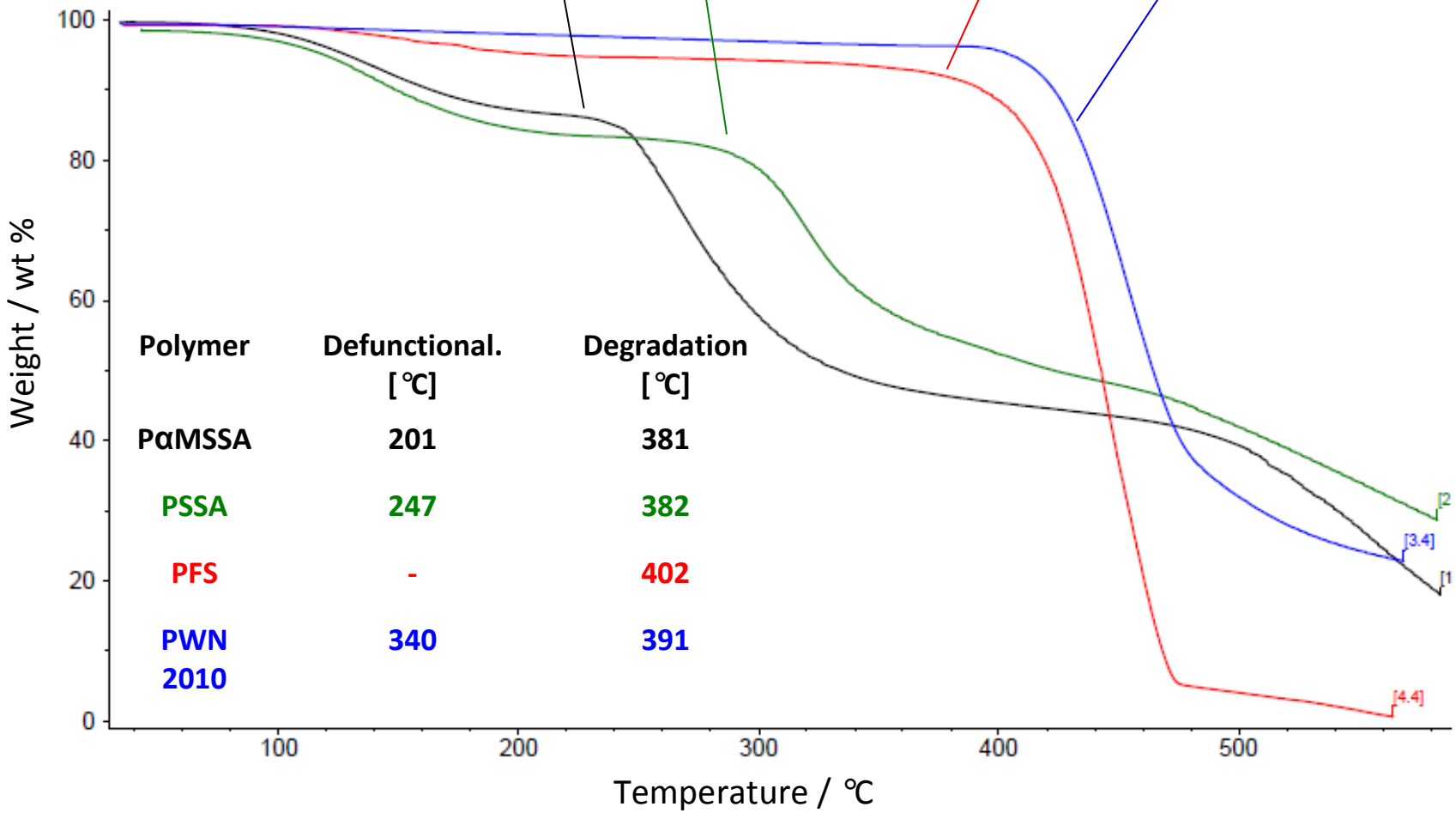
SAXS



Thermogravimetric analysis



PαMSSA PSSA PFS PWN2010



Polymer	Defunctional. [°C]	Degradation [°C]
PαMSSA	201	381
PSSA	247	382
PFS	-	402
PWN 2010	340	391

Phosphonic acid condensation

^{31}P solid-state NMR

Drying: 50 °C, p = 1 mbar, a week

Observing: Single resonance

Reason: free phosphonic function

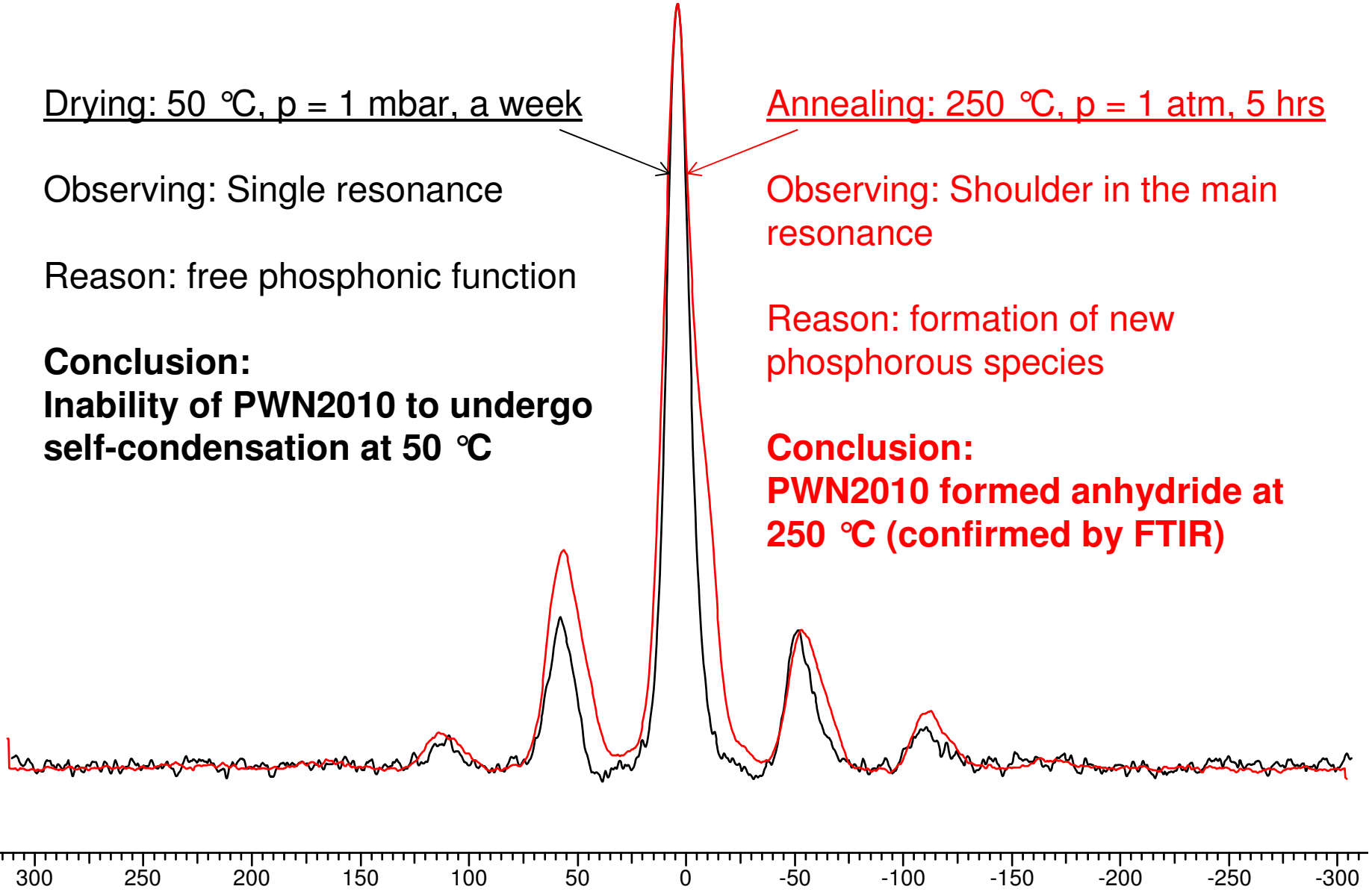
Conclusion:
Inability of PWN2010 to undergo self-condensation at 50 °C

Annealing: 250 °C, p = 1 atm, 5 hrs

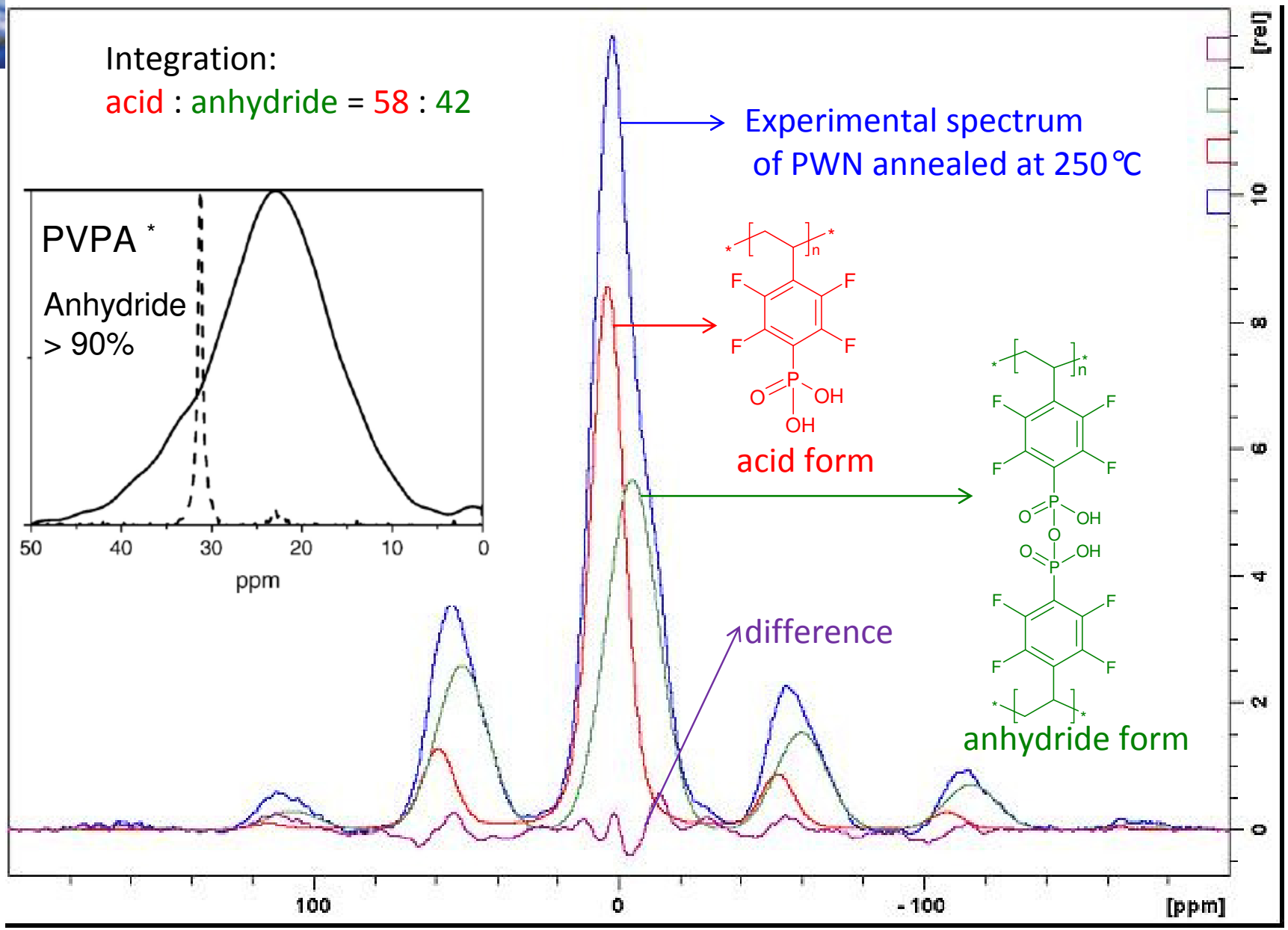
Observing: Shoulder in the main resonance

Reason: formation of new phosphorous species

Conclusion:
PWN2010 formed anhydride at 250 °C (confirmed by FTIR)



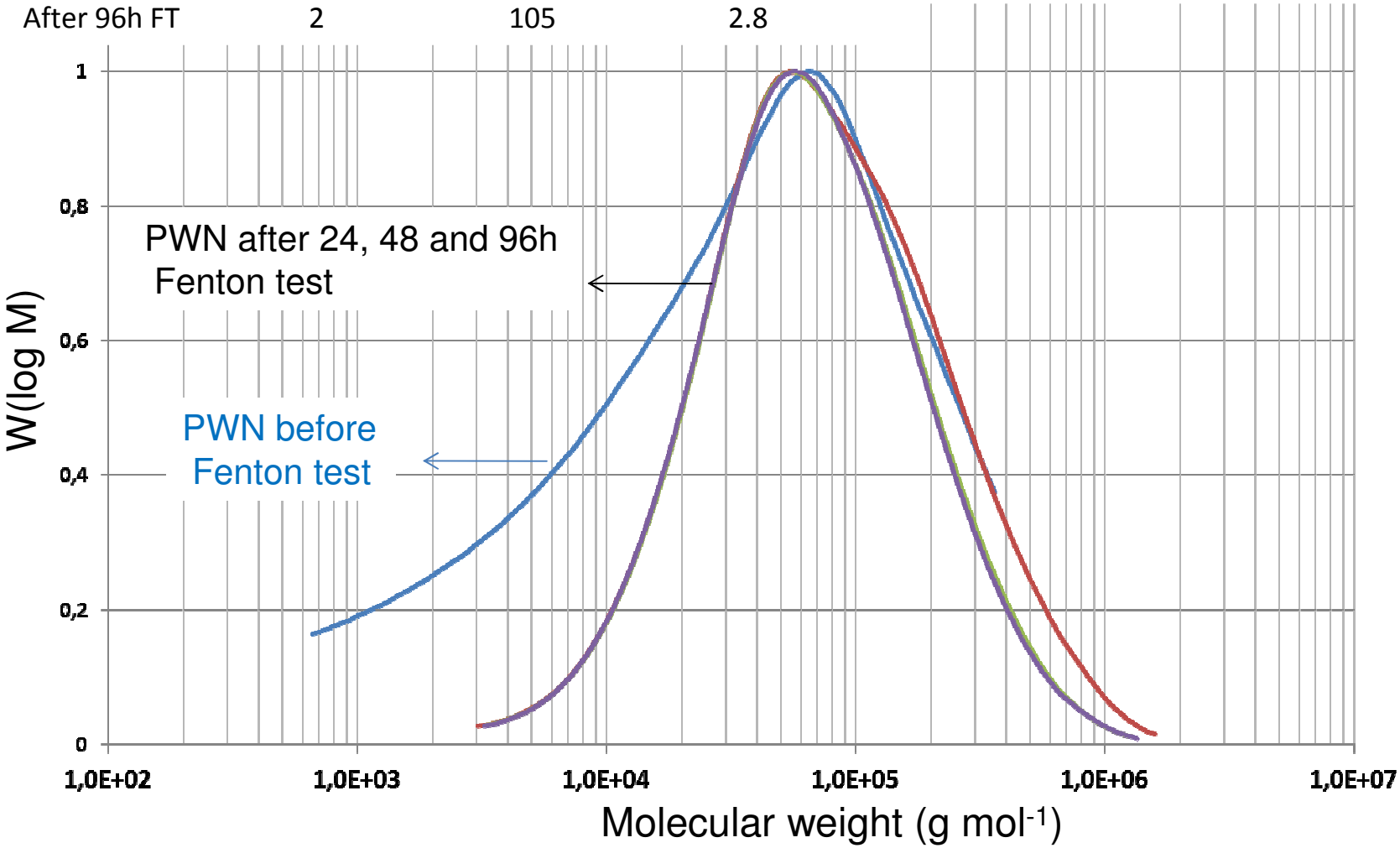
Simulation of ^{31}P CP/MAS NMR



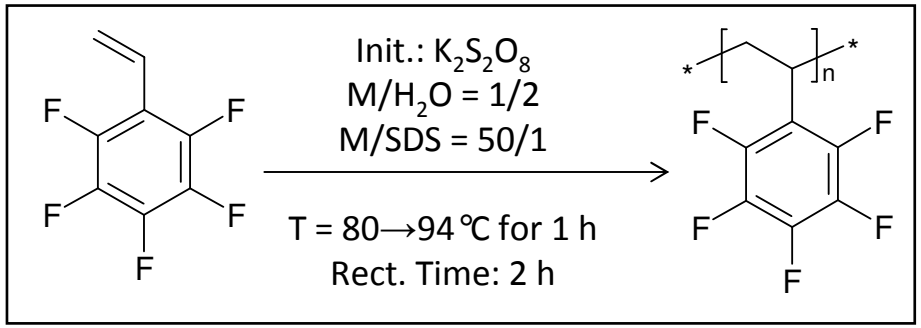
* A. Kaltbeitzel et al. *Solid State Ionics* 178 (**2007**) 469

Fenton test of PWN2010

PWN	Weightloss [wt%]	M_w / kDa	PDI
Before FT	-	67	7.4
After 24h FT	0	137	3.2
After 48h FT	0	106	2.8
After 96h FT	2	105	2.8

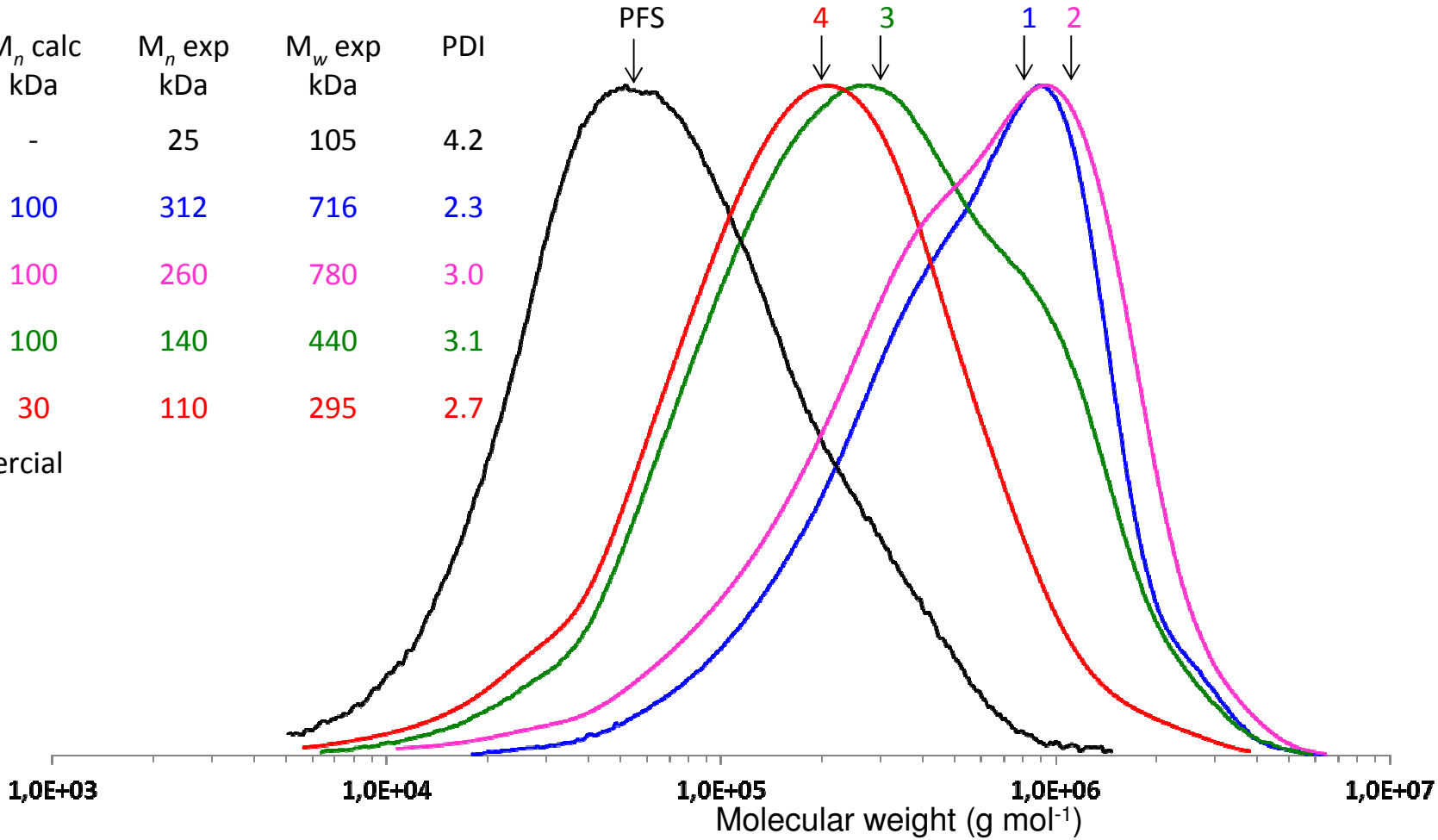


Emulsion polymerization of PFS

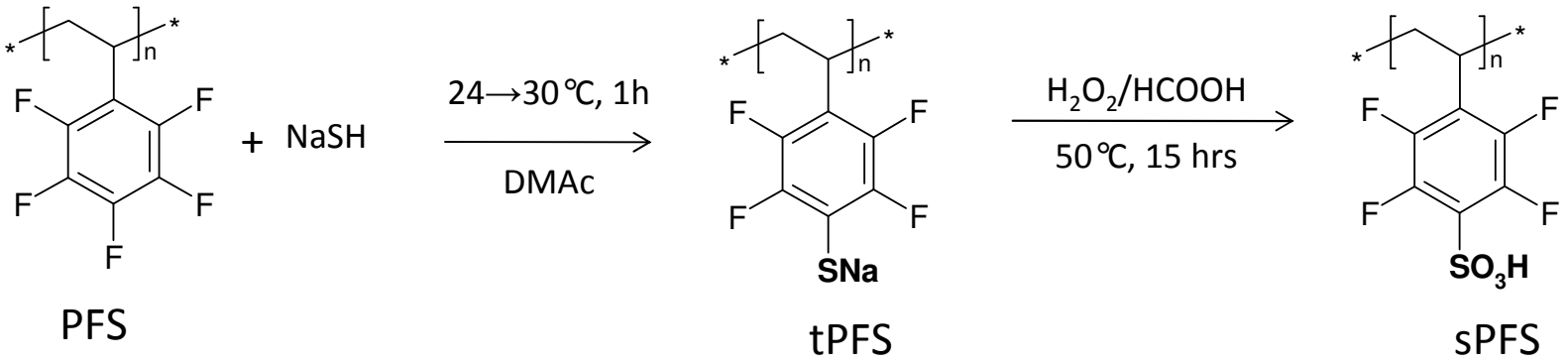


Name	M_n calc kDa	M_n exp kDa	M_w exp kDa	PDI
PFS*	-	25	105	4.2
1	100	312	716	2.3
2	100	260	780	3.0
3	100	140	440	3.1
4	30	110	295	2.7

*commercial



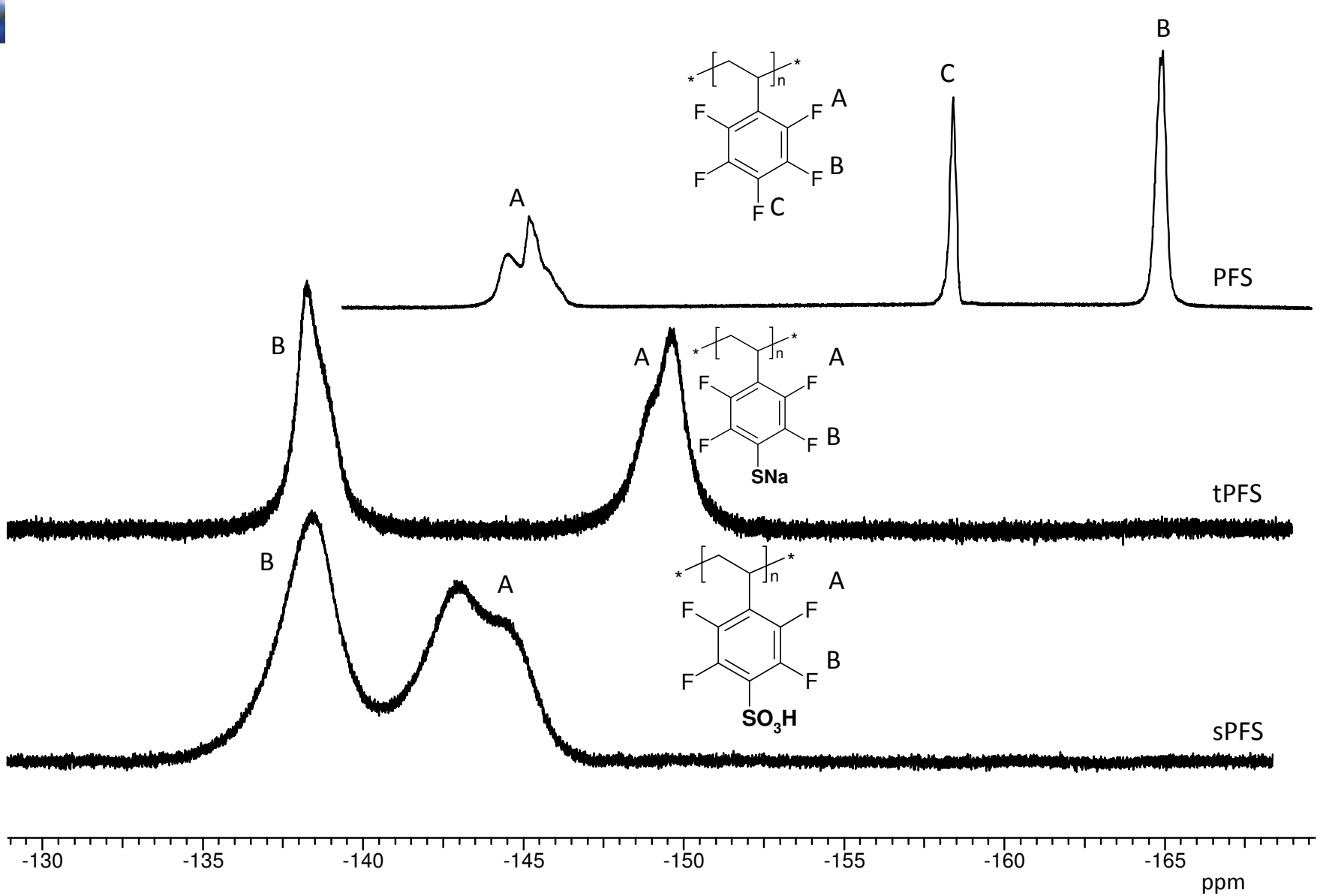
Sulfonation of PFS



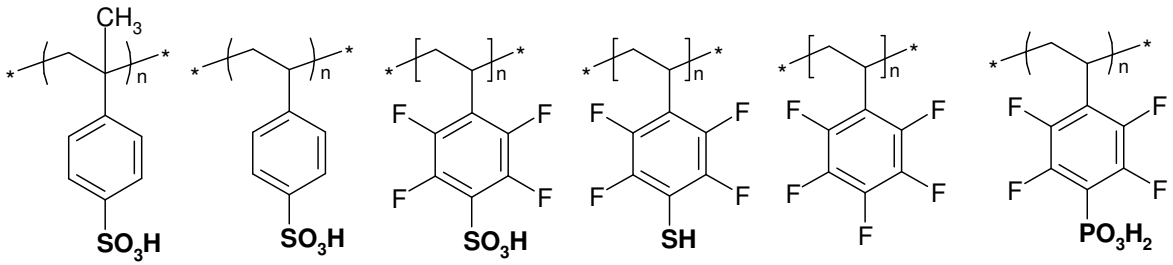
Characteristics:

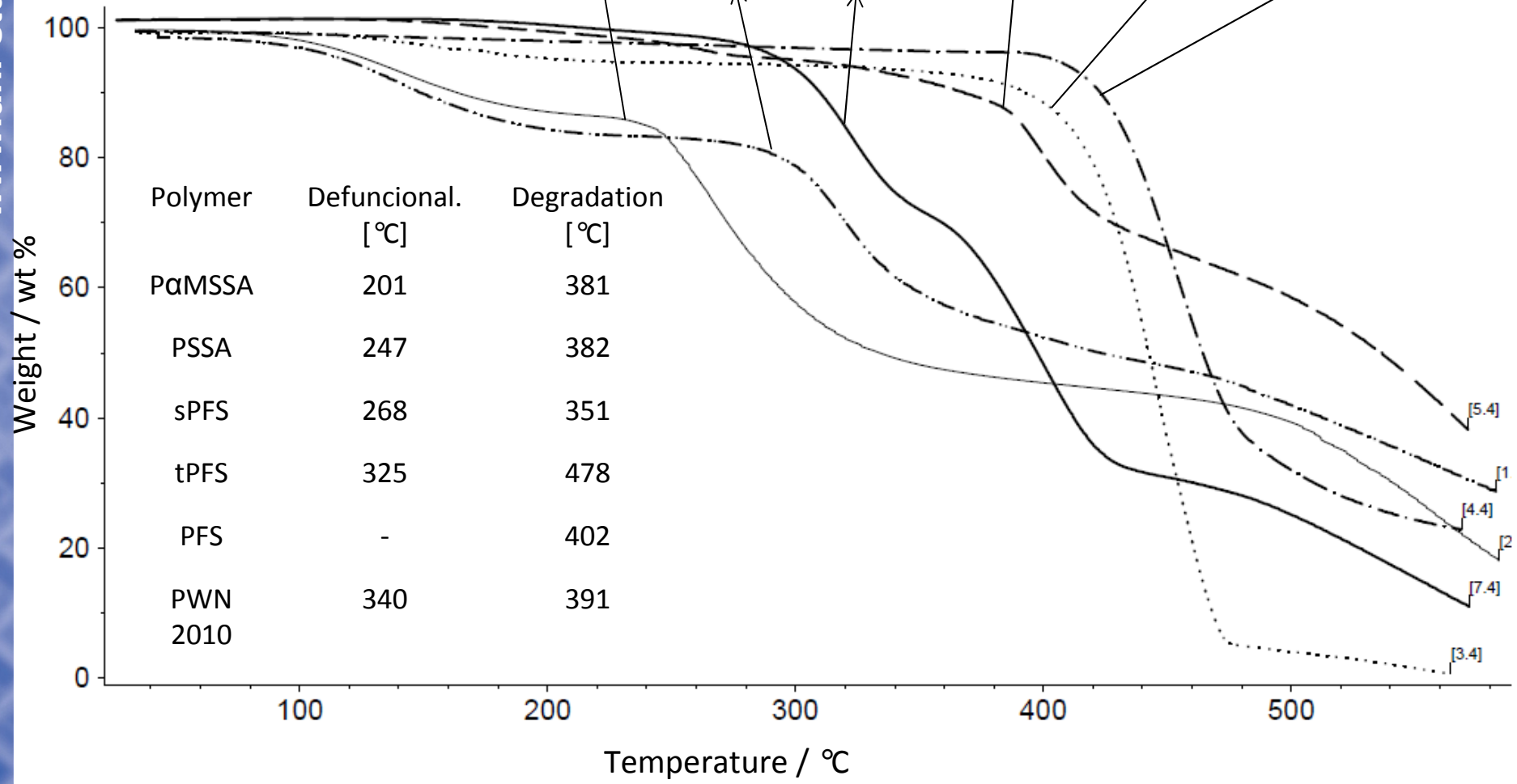
- sulfonation **100 %**
- IEC = **3.4 mmol g^{-1}** (calc. 3.9 mmol g^{-1})
- pK_a = **- 2** (PSSA: pK_a = - 0.5)
- resistance to heat up to **270 °C**
- molecular weight is unknown: sPFS is partially soluble only in DMSO

^{19}F NMR



Thermogravimetrical analysis





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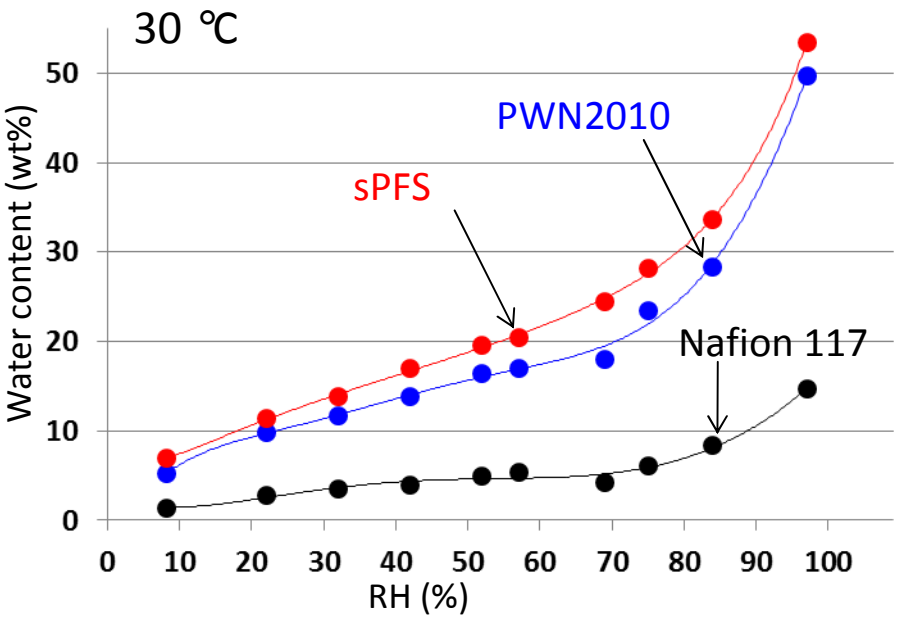
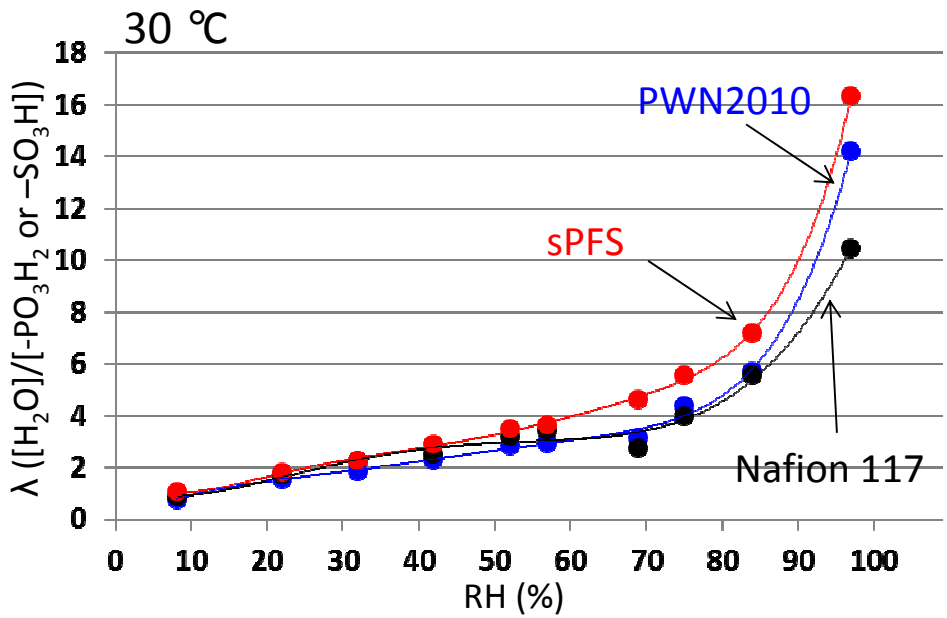
PSSA	247	382
sPFS	268	351
tPFS	325	478
PFS	-	402
PWN 2010	340	391

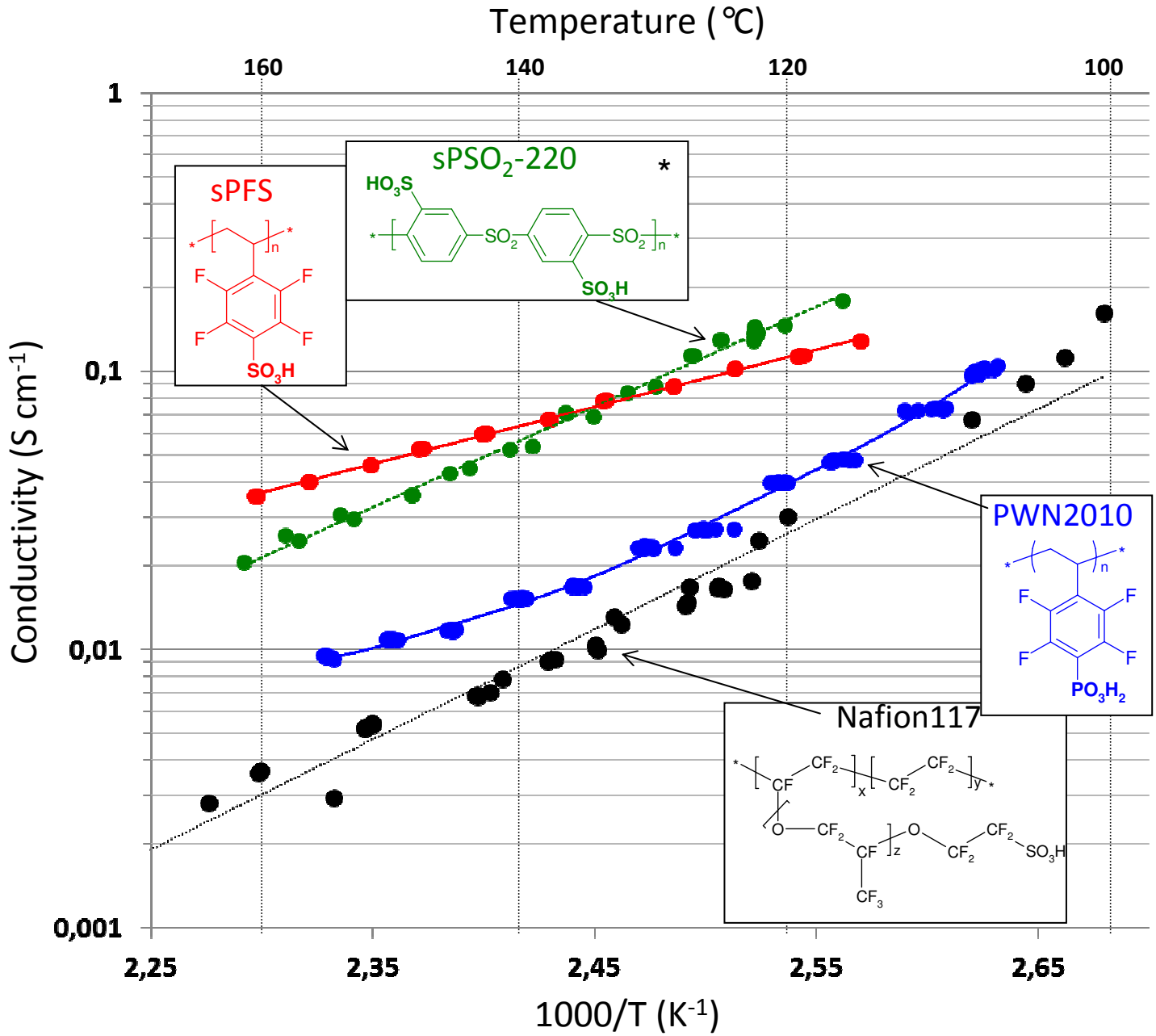
Hydration isotherms





The absolute higher water uptake of sPFS and PWN2010 is due to its higher number of functional group in compare to Nafion117.

Conductivity at 1atm water pressure



* M. Schuster *et al Macromolecules* ***2009,*** 42, 3129.

Summary & Conclusions

❖ Phosphonated poly(pentafluorostyrene) with phosphonation degree above 90% is obtained

- The high conductivity (σ = 0.1 S cm^{-1} at 110 °C):
- Lamellar structuring (SAXS).
- The reduced formation of anhydrides (^{31}P MAS NMR)
- Resistance to radical attack.

❖ Poly(pentafluorostyrene) was obtained by emulsion polymerization

- Molecular weight (GPC): up to 800 kDa
- Control over molecular weight

❖ Sulfonated poly(pentafluorostyrene) is obtained with 100% sulfonation degree.

- Ion conductivity (σ = 50 mS cm^{-1} at 150 °C) is making this material one of the best ion-conducting polymer.

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Thank you!