
Derivatization XPS of surface OH and NH_x groups with TFAA

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Content

- The challenge
- Chemical derivatization
- Determination of OH groups
- Determination of NH_x groups
- Conclusion

Surface analysis of polymers after plasma treatment

polymers are chemically rather stable materials

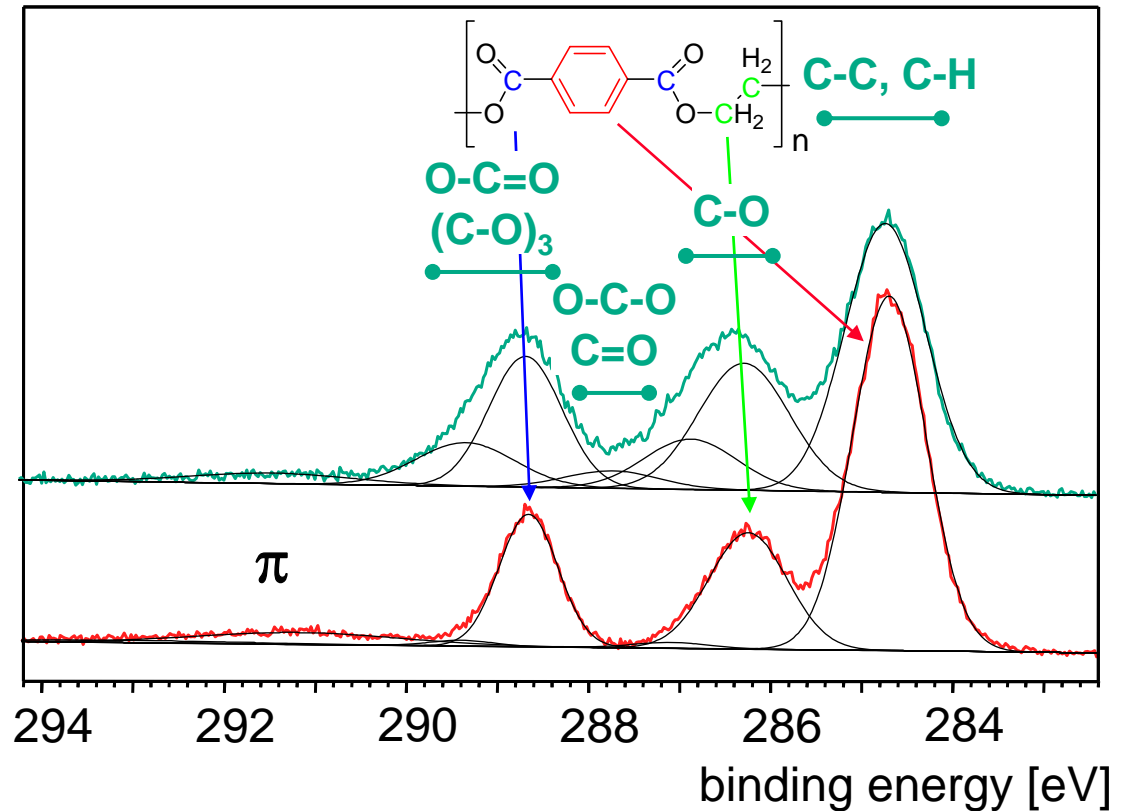
PET
poly(ethylene terephthalate)

➤ activation

reactivity $\sim \frac{1}{\text{selectivity}}$

chemically heterogeneous surface

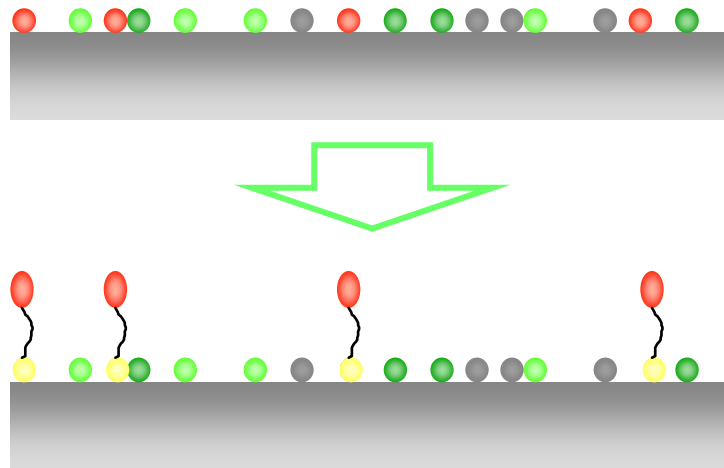
plasma treatment



Derivatization - Labelling

principle

- coupling of functional molecules on a certain type of functional group



demands

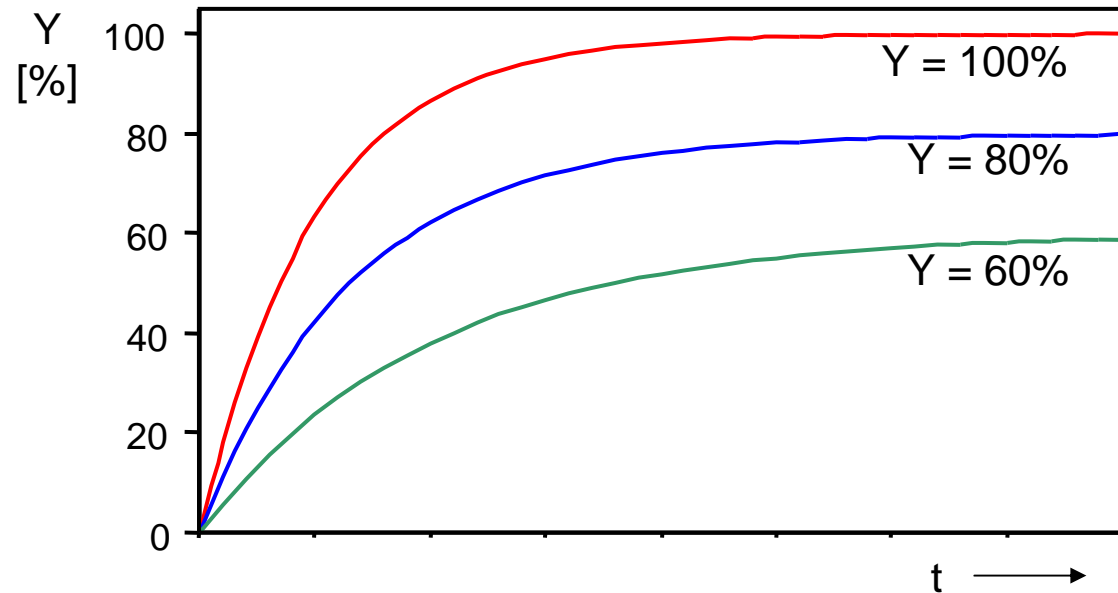
- selective for a given surface
- high yield
- not too low rate
- no unspecific influence on surface



Demands on labelling reactions (A)

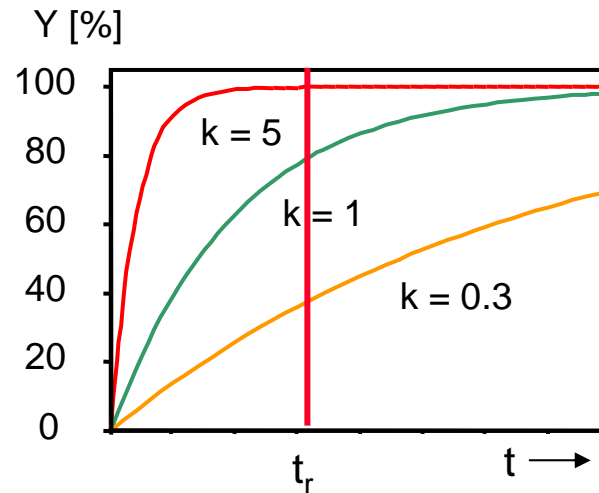
yield

- reactions known from organic chemistry
- usually high excess of the agent, in particular in liquid-phase reactions
- gas phase reactions at low p : limited by diffusion



Demands on labelling reactions (B)

rate



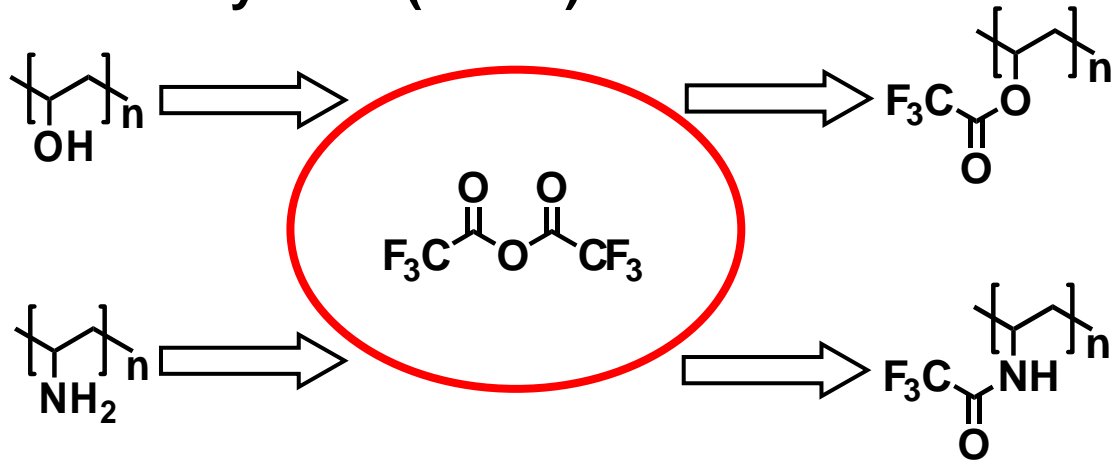
unspecific influence

- swelling, dissolution
- small unspecific effect: gas phase reactions
- but: what is the state we need to analyze?
 - surface as formed
 - or
 - surface as seen by an application

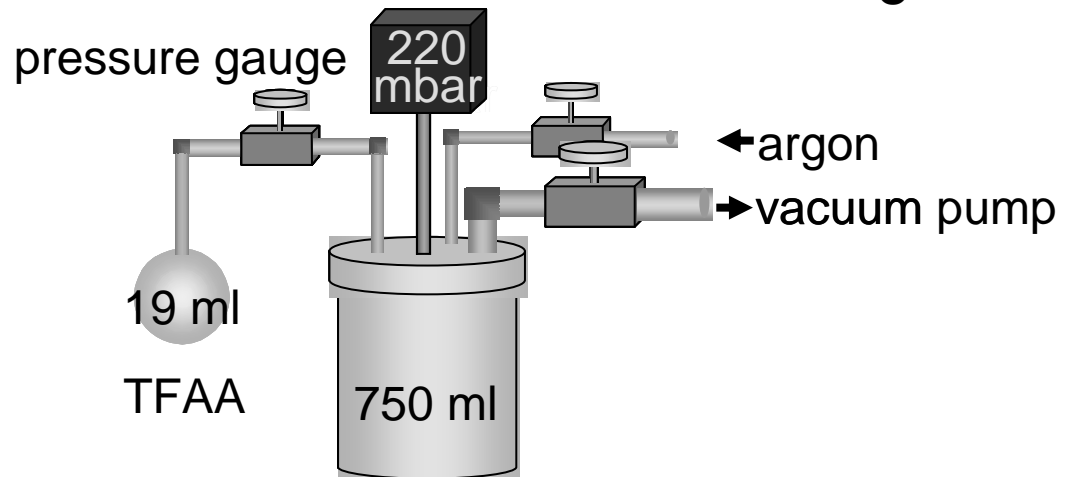


Reaction with trifluoroacetic anhydride (TFAA)

reaction

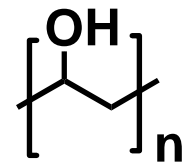
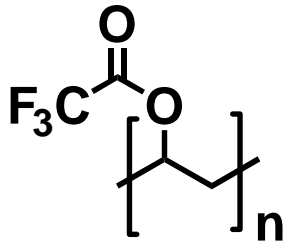


apparatus

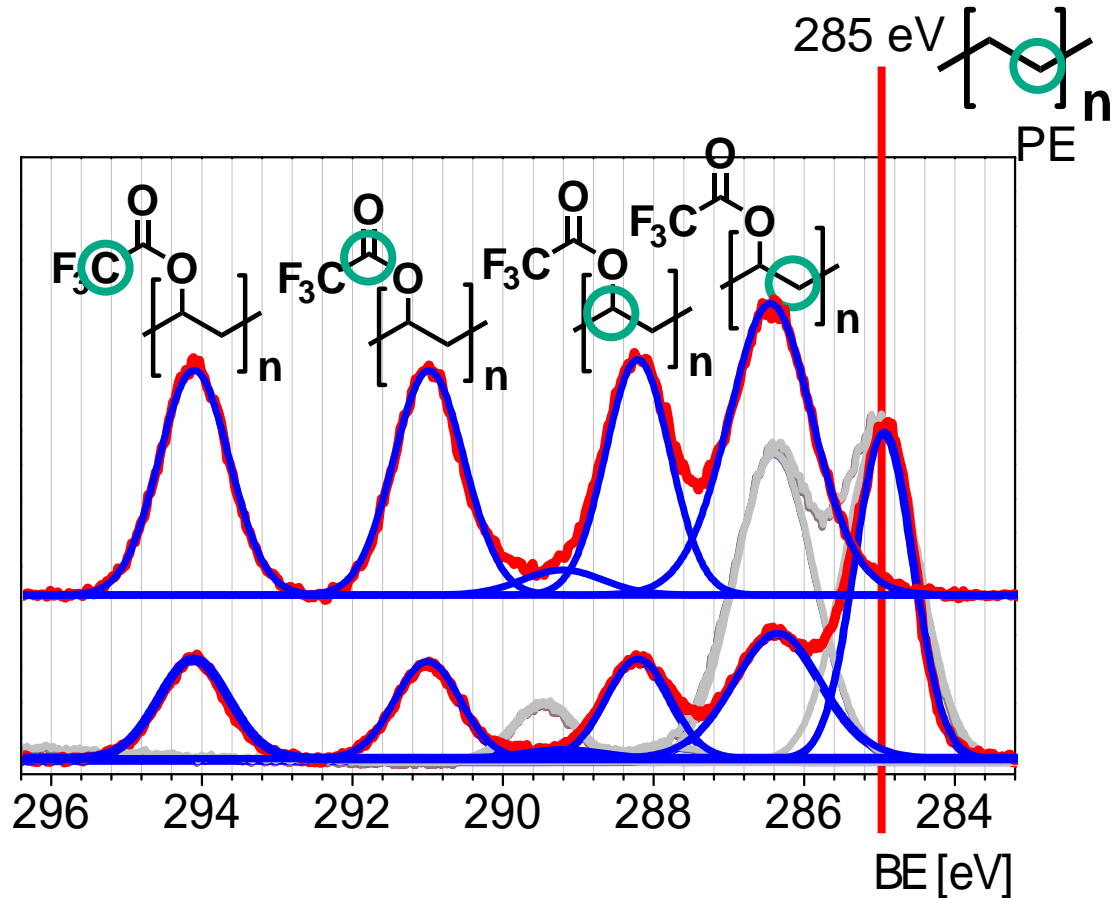


Which is the best binding energy reference?

PVTFA



PVA

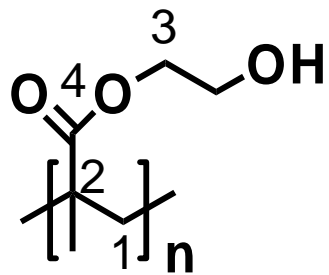
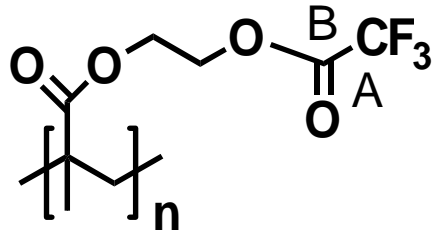


➔ BE CF₃: 294.2 eV

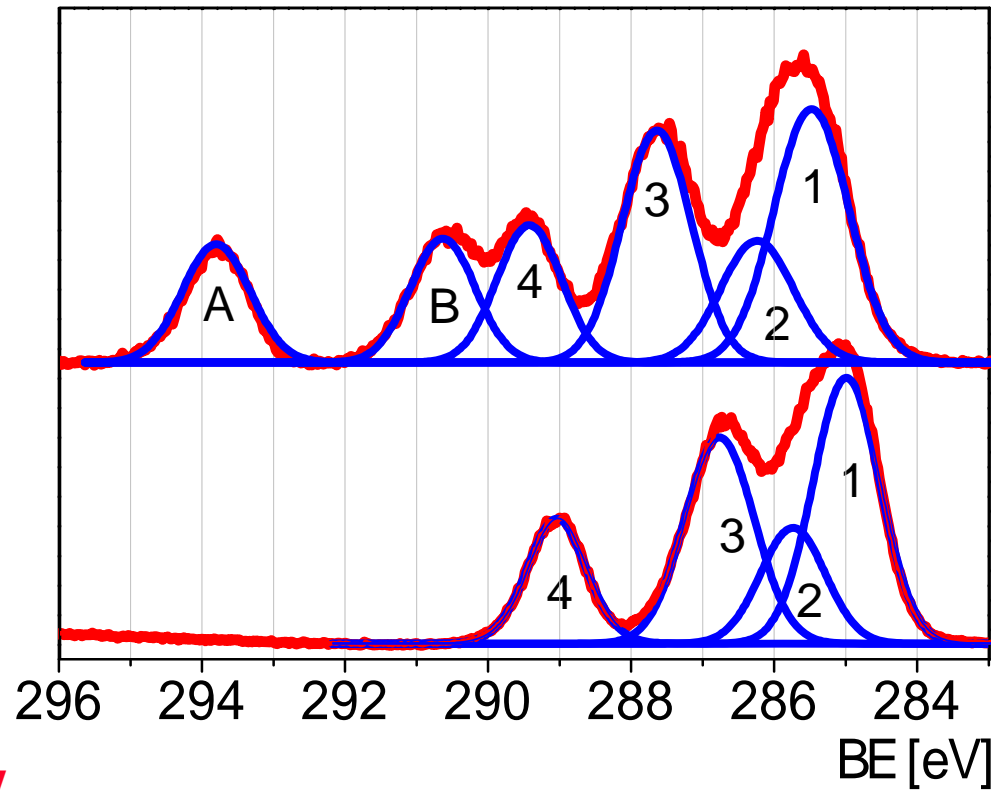


Determination of OH groups in PHEMA

PHEMA-TFAA



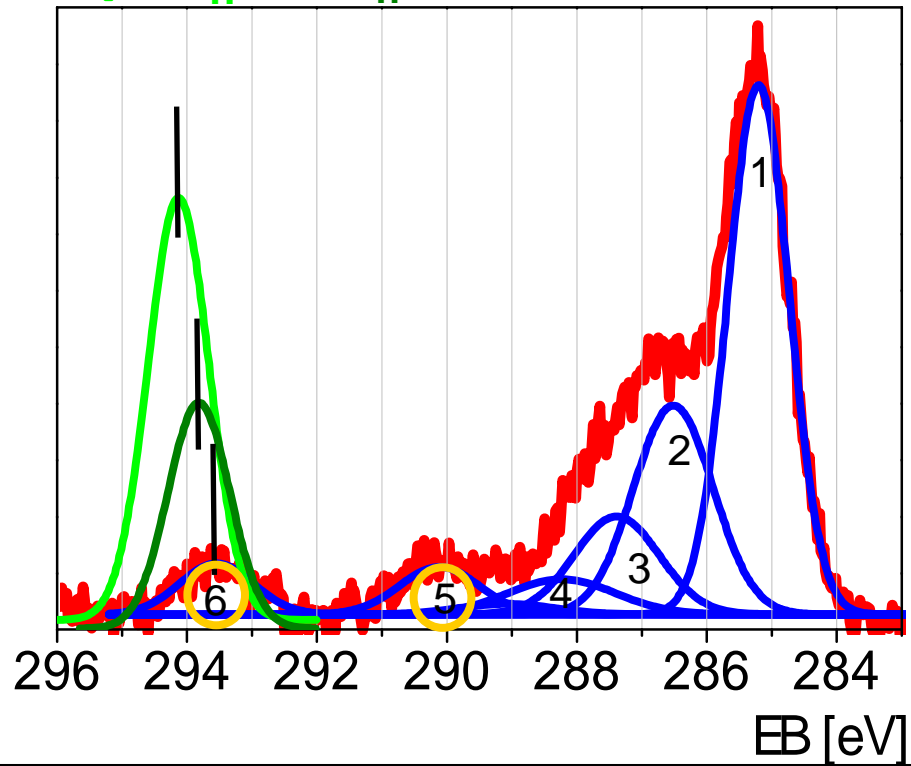
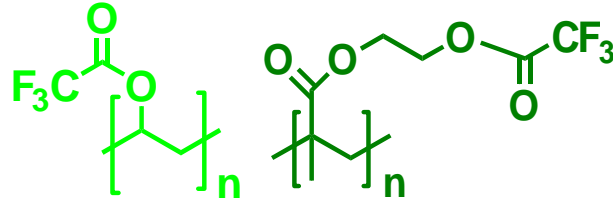
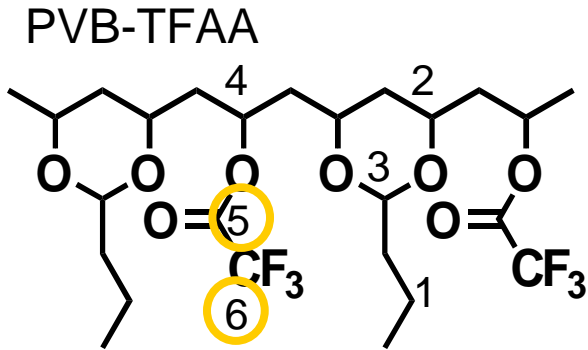
PHEMA



➔ BE CF₃: 293.8 eV



Isolated OH groups in PVB

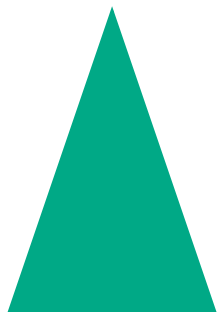


➔ BE CF₃: 293.6 eV

Overview OH-groups

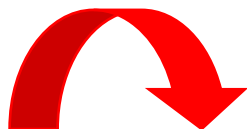
Distance between

CF₃



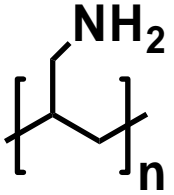
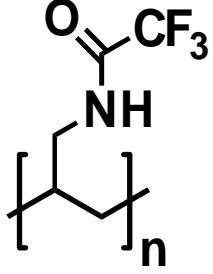
polymer	BE CF ₃ [eV]	BE CF ₃ - ester 1 [eV]	BE CF ₃ - ester 2 [eV]
PVA-TFAA	294.3	291.2	288.5
PHEMA-TFAA	293.8	290.6	287.6
PVB-TFAA	293.6	290.4	288.1

Amines reacts also with TFAA
forming an amide

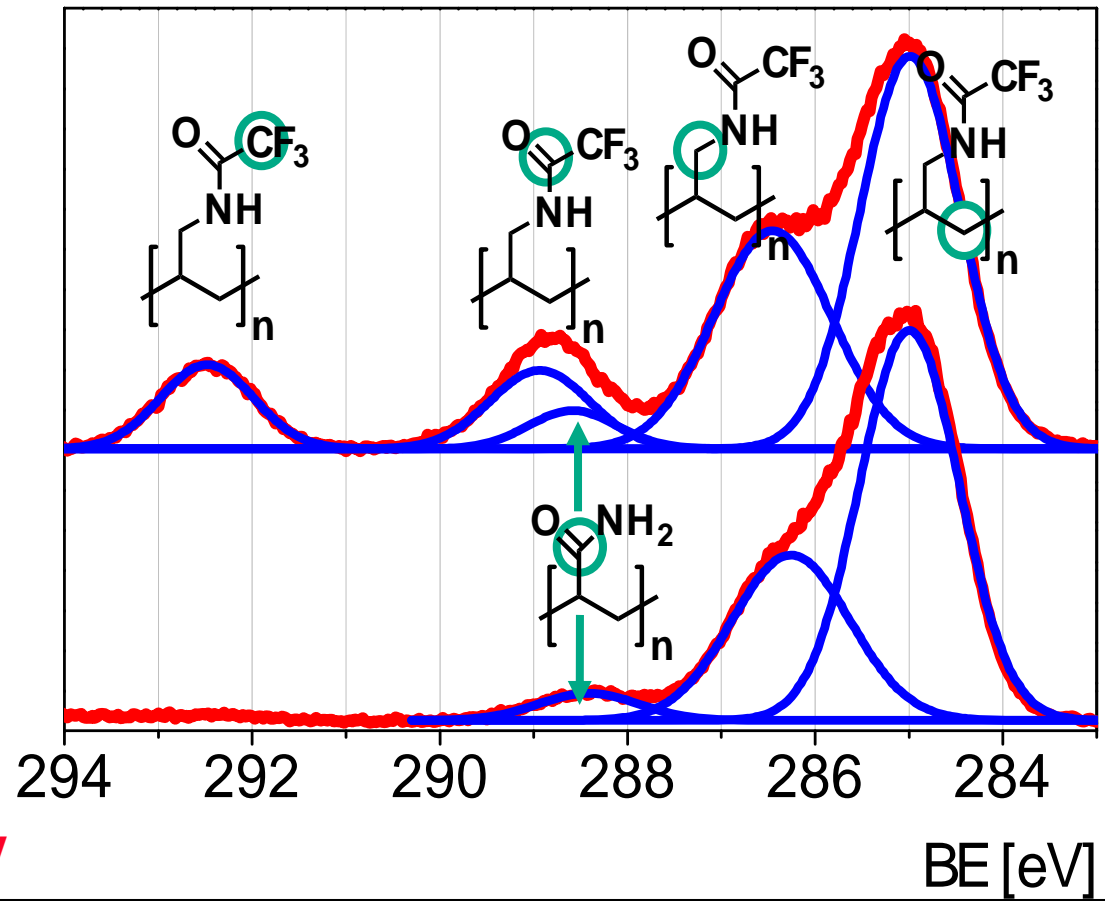


Determination of primary amine groups in PAAm

PAAm-TFAA



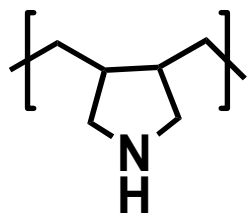
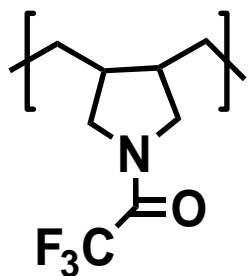
PAAm



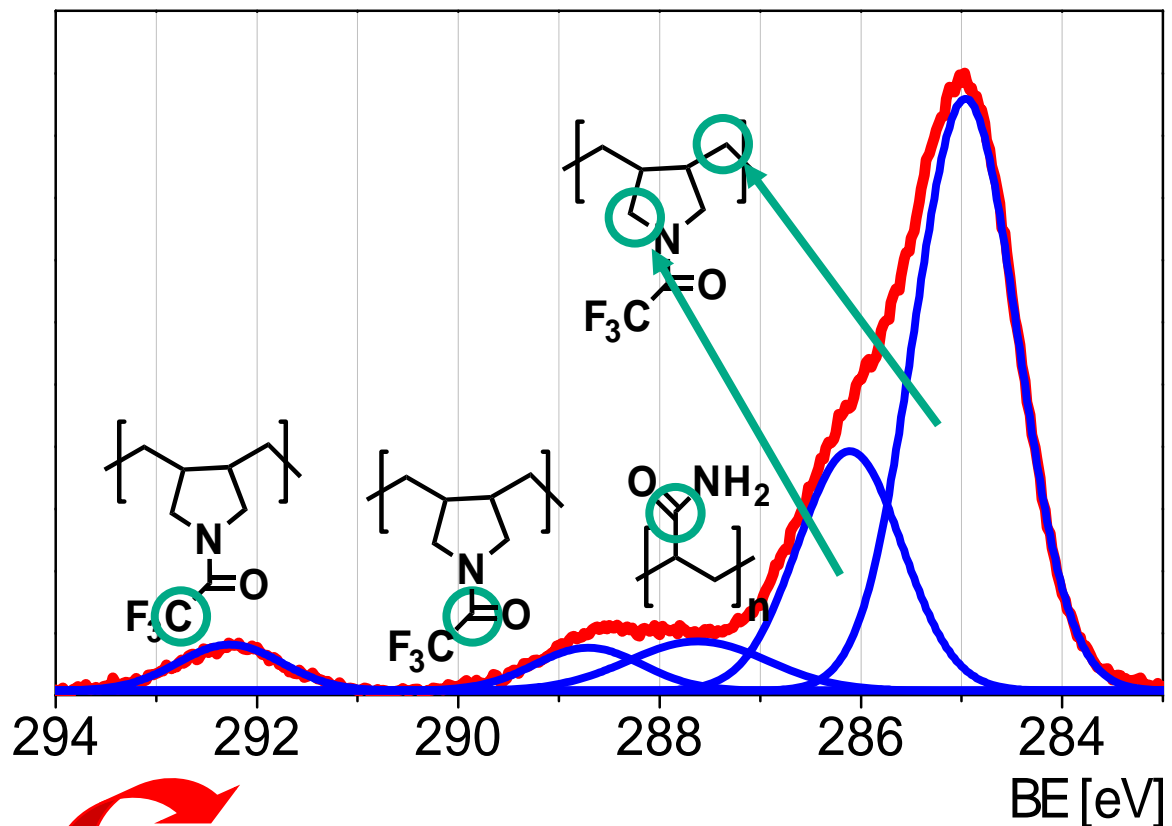
➡ BE CF₃: 292.5 eV

Determination of secondary amine groups in PDAAm

PDAAm-TFAA



PDAAm

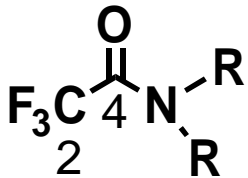
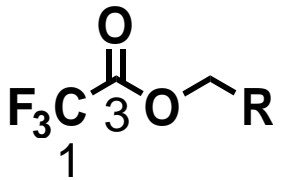


BE CF_3 : 292.2 eV

BE CF_3 amines < BE CF_3 hydroxy groups

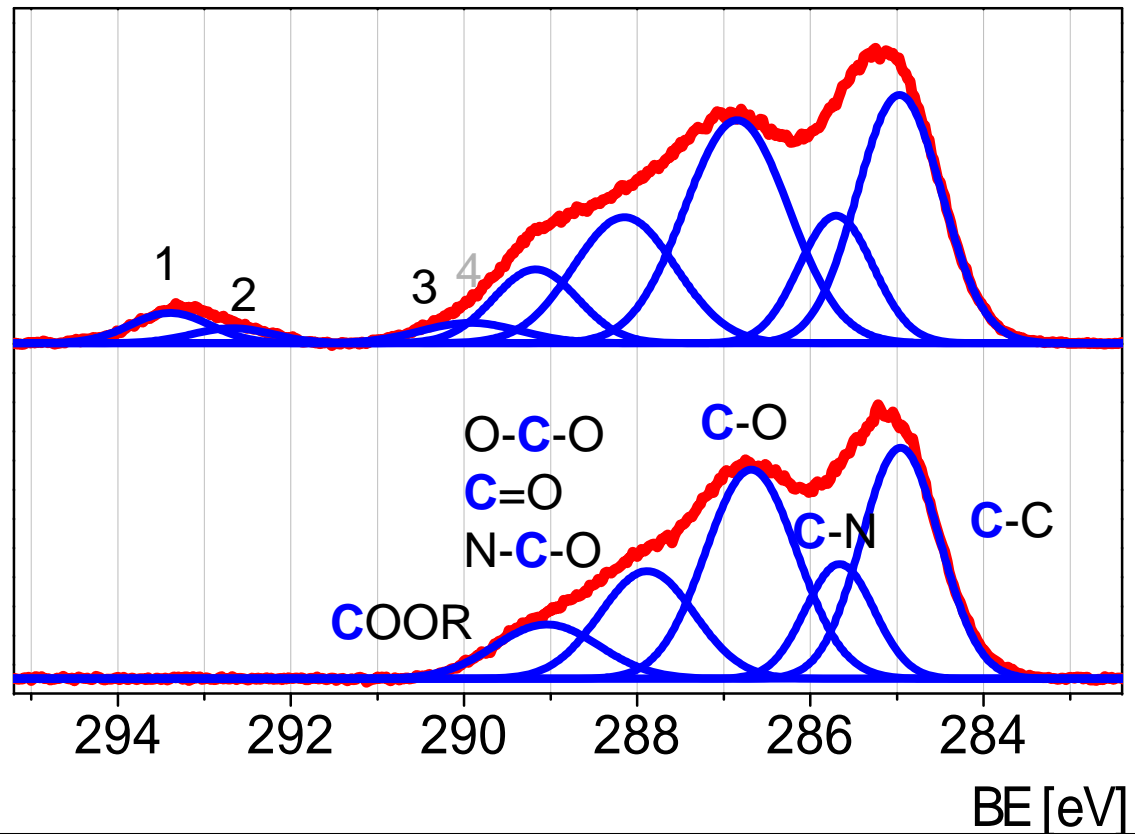
Application: VITO plasma polymer

- nitrogen np-plasma
- ethyl acetat

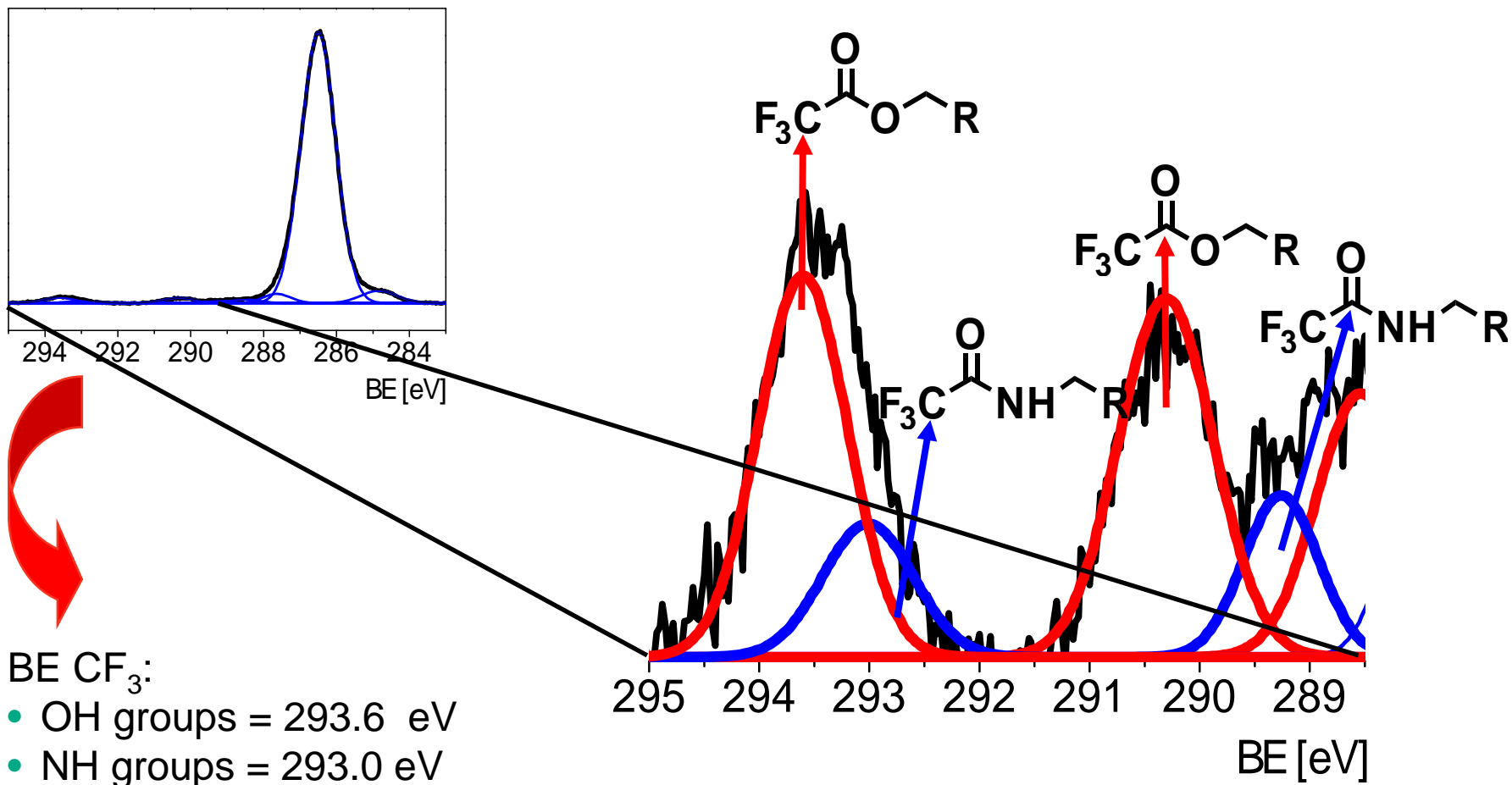


BE CF_3 :

- OH groups = 293.3 eV
- NH_x groups = 292.6 eV



Application: Analysis of network structure



Conclusion

- parallel determination of hydroxy & amine groups
- densely packed OH 294.2 eV
- isolated OH 293.6 eV
- NH₂ 292.5 eV

Calculation of functional groups concentration [X]:

$$[X] = \frac{\frac{1}{3} \cdot [F]}{[C] - \frac{2}{3} \cdot [F]} \cdot 100\%$$

$$[X] = \frac{[CF_3]}{100 - 2 \cdot [CF_3]} \cdot 100\%$$



Who has supported this work?

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Thank you very much for your attention!

