

Polymer surface modification with mono-functional groups of different type and density

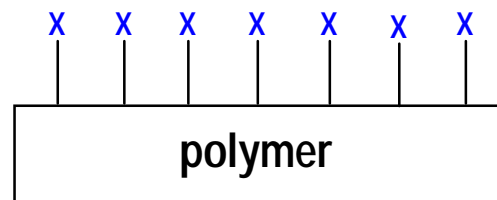
J. Friedrich

W. Unger, A. Lippitz, I. Retzko (BAM-VIII.23),
G. Kühn, R. Mix, A. M.-Plath, R.-D. Schulze,
St. Weidner, V. Gerstung (BAM-VI.3),
A. Ghode (Indien), I. Koprinarov (USA),
Sh. Geng (China).....

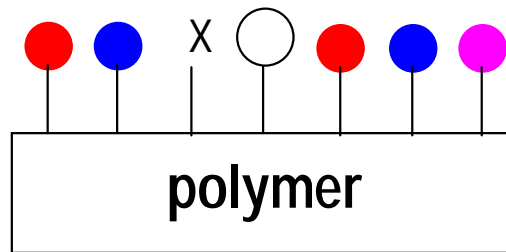


General intention

plasma-enhanced formation of
monosort functionalized polymer surfaces

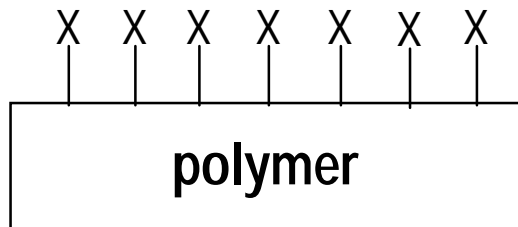


Functionalization of polymer surfaces by plasma modification



Unspecific functionalization

e.g. formation of different O functional groups by exposure to oxygen plasma

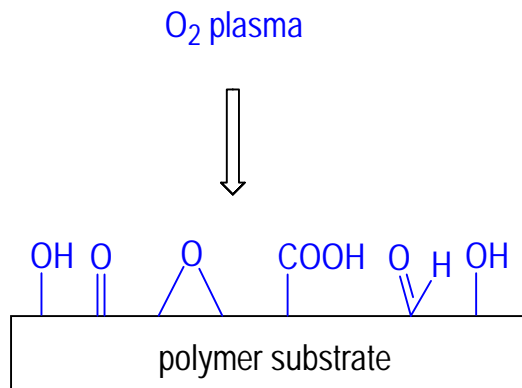


Specific functionalization

e.g. formation of functional groups of one type by bromination, combination with chemical processes, pulsed plasma polymerization of functional groups carrying monomers

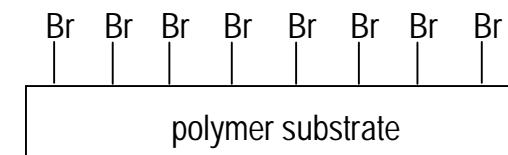
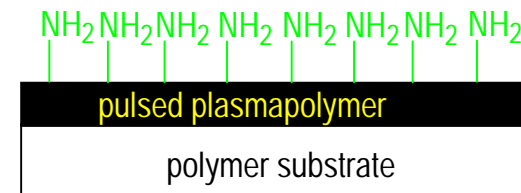
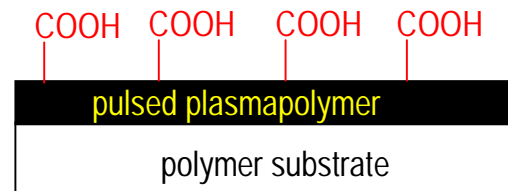
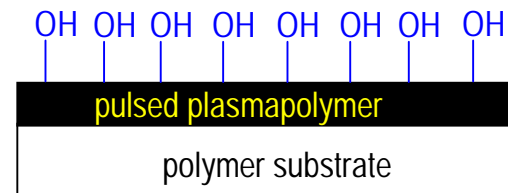
Plasmachemical surface functionalization of polymers

Unspecific and specific functionalization



*unspecific surface functionalization
-old process-*

Result: maximal 25-28 different (multifunctional) O functional groups per 100 C atoms at the polymer surface



*specific surface functionalization
-new process-*

Result: maximal 18-40 monofunctional (monosort) groups per 100 C atoms at the polymer surface

Problems with the unspecific functionalization

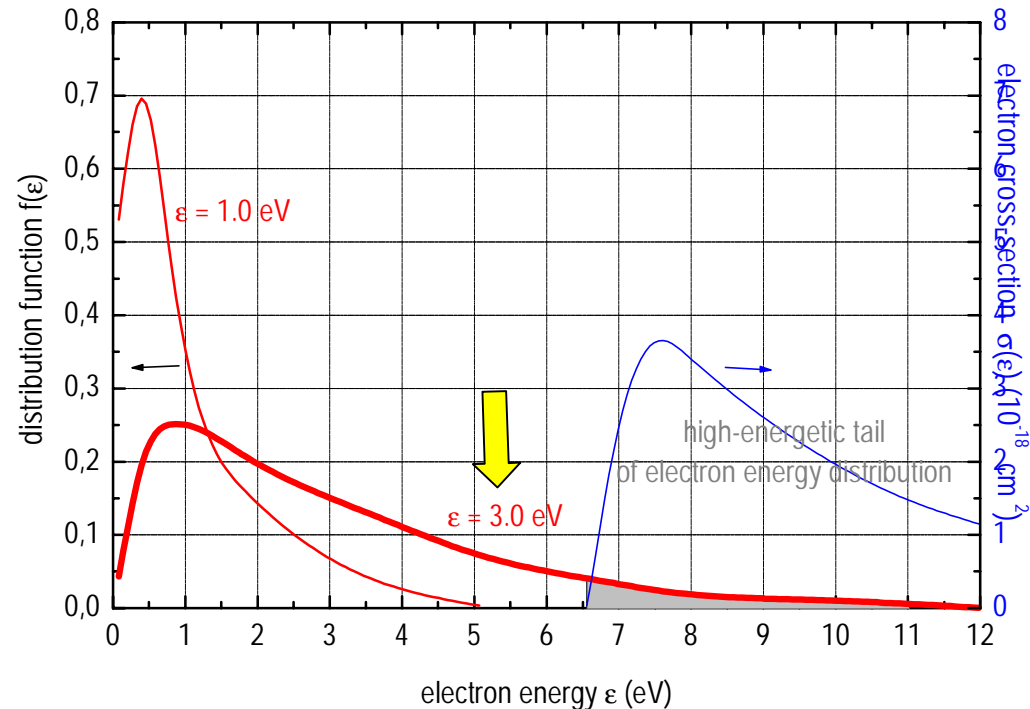
Broad variety of different functional groups is formed,
which is derived from the composition of the plasma gas

The cause of the broad product spectrum is the excess of energy in the plasma, which is much higher than the activation energy of an ordinary chemical reaction

energy distribution of electrons in the non-isothermal plasma



binding energies in organic molecules



↔ radical chain propagation (polymerization of styrene)

↔ C-H and C-C bond dissociation
(radical formation and crosslinking)

↔ ionization

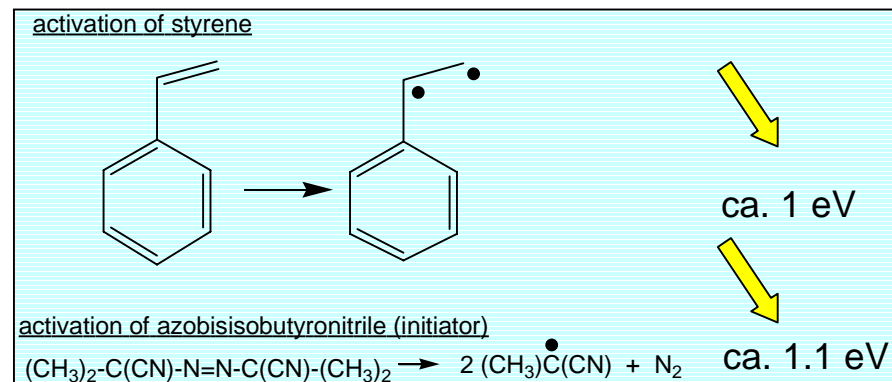
↔ cracking of aromatic rings
(„polymerization“ of benzene)

Elemental processes in the non-isothermal plasma

Collision processes

1	$e^- + A$	\Rightarrow	$A^+ + e^-_1 + e^-_2$	ionization
2	$e^- + A$	\Rightarrow	$A^* + e^-_1$	excitation
3	$A^* + B$	\Rightarrow	$A + B^+ + e^-_1$	Penning ionization
4	A^*	\Rightarrow	$A + h\nu$	radiative desactivation
5	$A^+ + B$	\Rightarrow	$A + B^+$	re-charging
6	$A^+ + e^- + M$	\Rightarrow	$A + M^*$	recombination by three body collision
7	$A^+ + e^-$	\Rightarrow	$A + h\nu$	radiative recombination
8	$A^+ + B$	\Rightarrow	AB^+	ion-molecule reaction
9	$A^* + B$	\Rightarrow	$AB^+ + e^-$	Hornbeck-Molnar process
10	$ABCD^+ + e^-$	\Rightarrow	$ABCD^*$	recombination with internal excitation of vibrations
11	$AB^+ + e^-$	\Rightarrow	$A^* + B$	dissociative recombination
12	$A^+ + B^- + M$	\Rightarrow	$AB + M^*$ or $A + B + M^*$	recombination of ions
13	$A + e^- (+M)$	\Rightarrow	$A^- (+ h\nu, M^*)$	formation of negative ions
14	$AB + e^-$	\Rightarrow	$A^+ + B^- + e^-_1$	Ion-pair formation (at high kinetic energies)

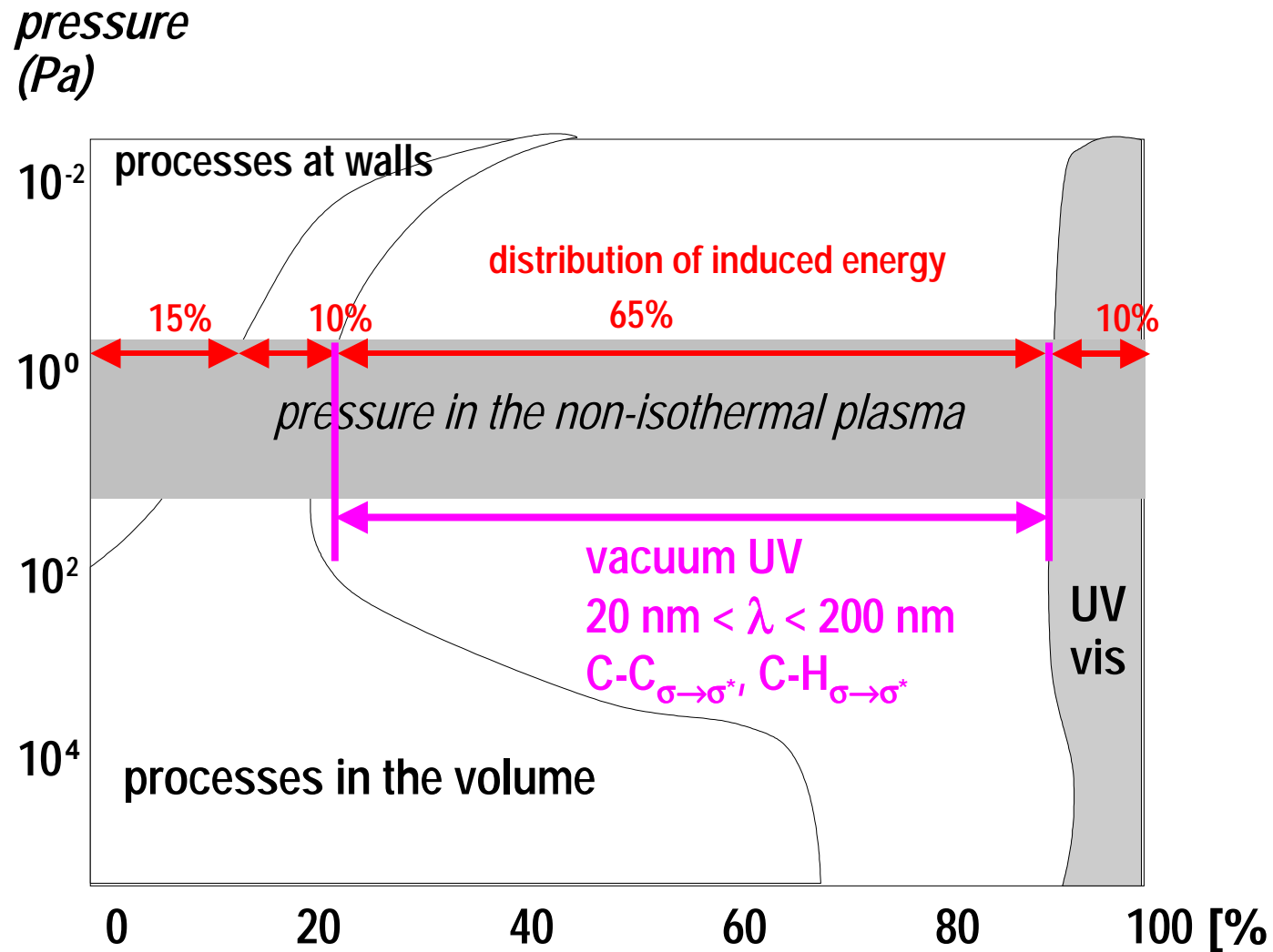
$1 e^- + A \Rightarrow A^+ + e^-_1 + e^-_2$	ionisation energy (eV)	dissociation energy (eV)
CF ₄	17.8	5.3
CHBr ₃	10.5	2.4 (Br), 4.0 (H)
CH ₄	13.0	4.5
C ₂ F ₂	10.1	4.2
C ₂ H ₂	11.5	5.0
C ₂ H ₄	10.6	4.7
CH ₃ COOH	10.4	3.9 (OH), 4.9 (H)
CH ₃ CH ₂ -OH	10.6	3.9 (OH), 4.4 (H)
C ₆ H ₆	9.3	4.4 (H), 11.5 (C=C)
C ₆ H ₁₄	10.4	4.4 (H)



The further chain propagation is exothermic, needs no further energy !!!!

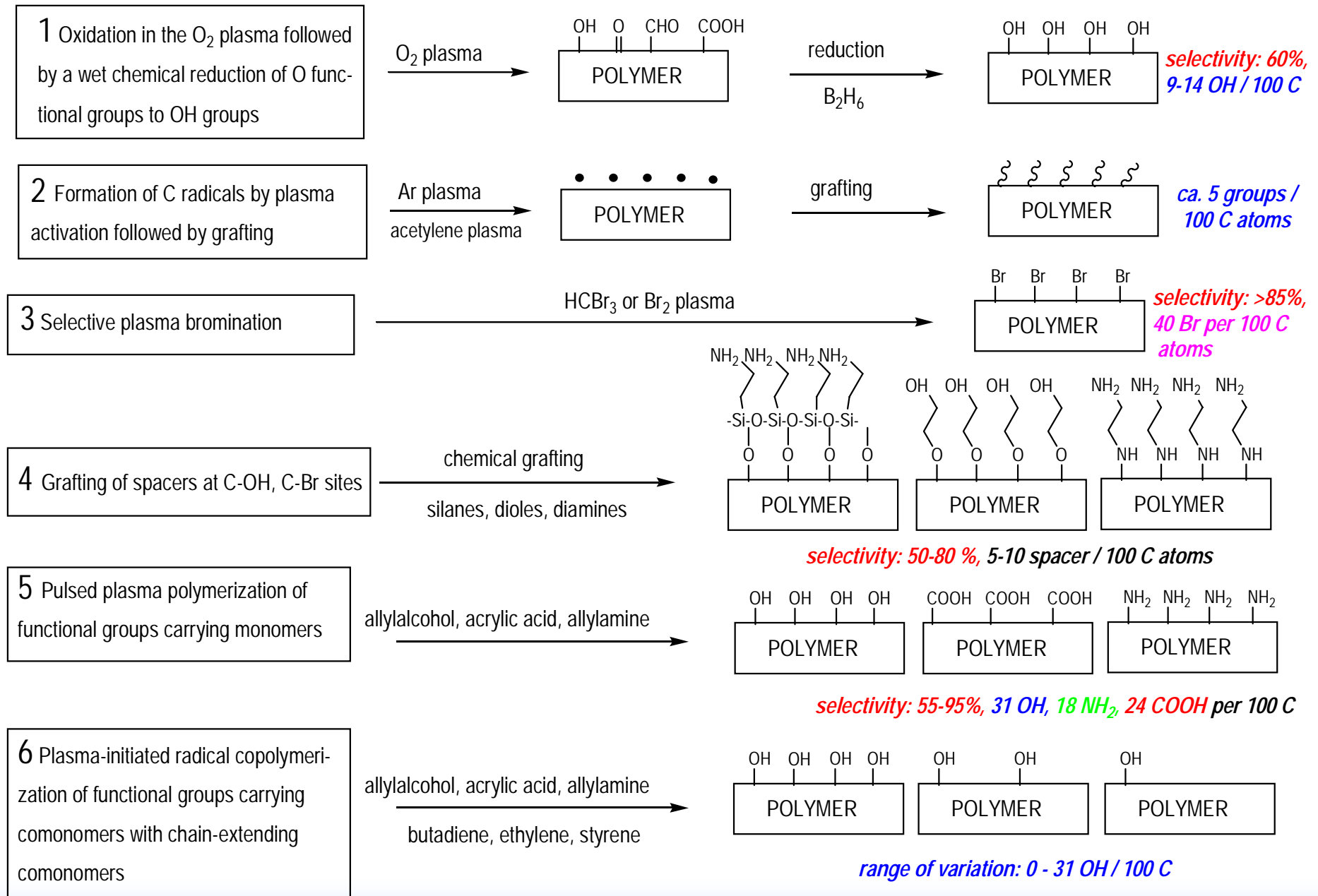
Elemental processes in the non-isothermal plasma

energy consumption



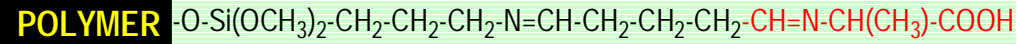
Percentage of consumed energy in the plasma referred to the power-input

Available ways to produce monosort functionalized polymer surfaces

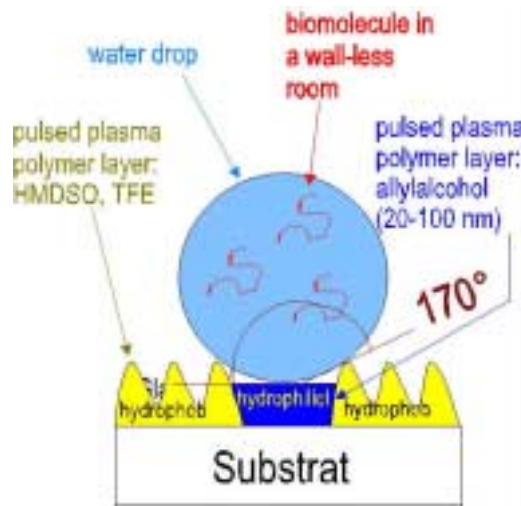


Applications

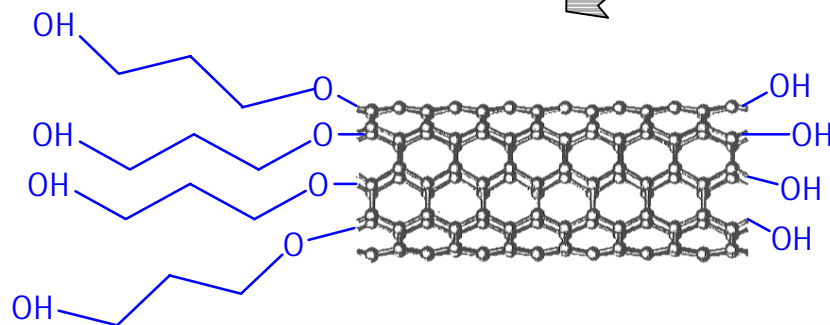
Applications of functionalized polymer surfaces



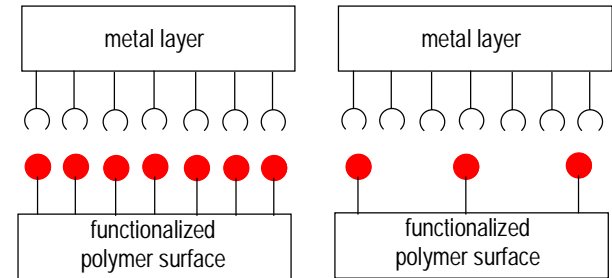
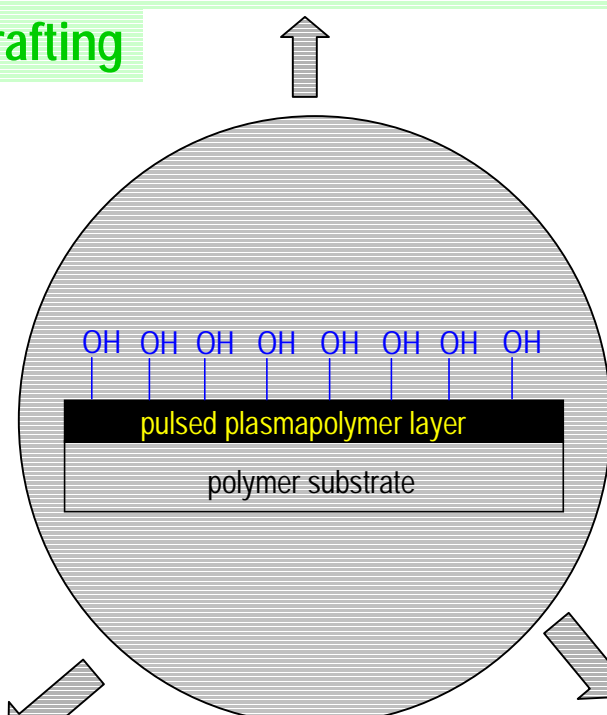
biomolecule grafting



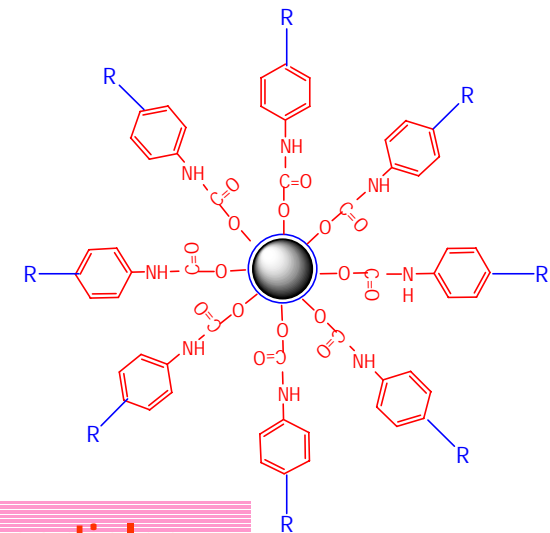
water drop reactor



modification of C nanotubes



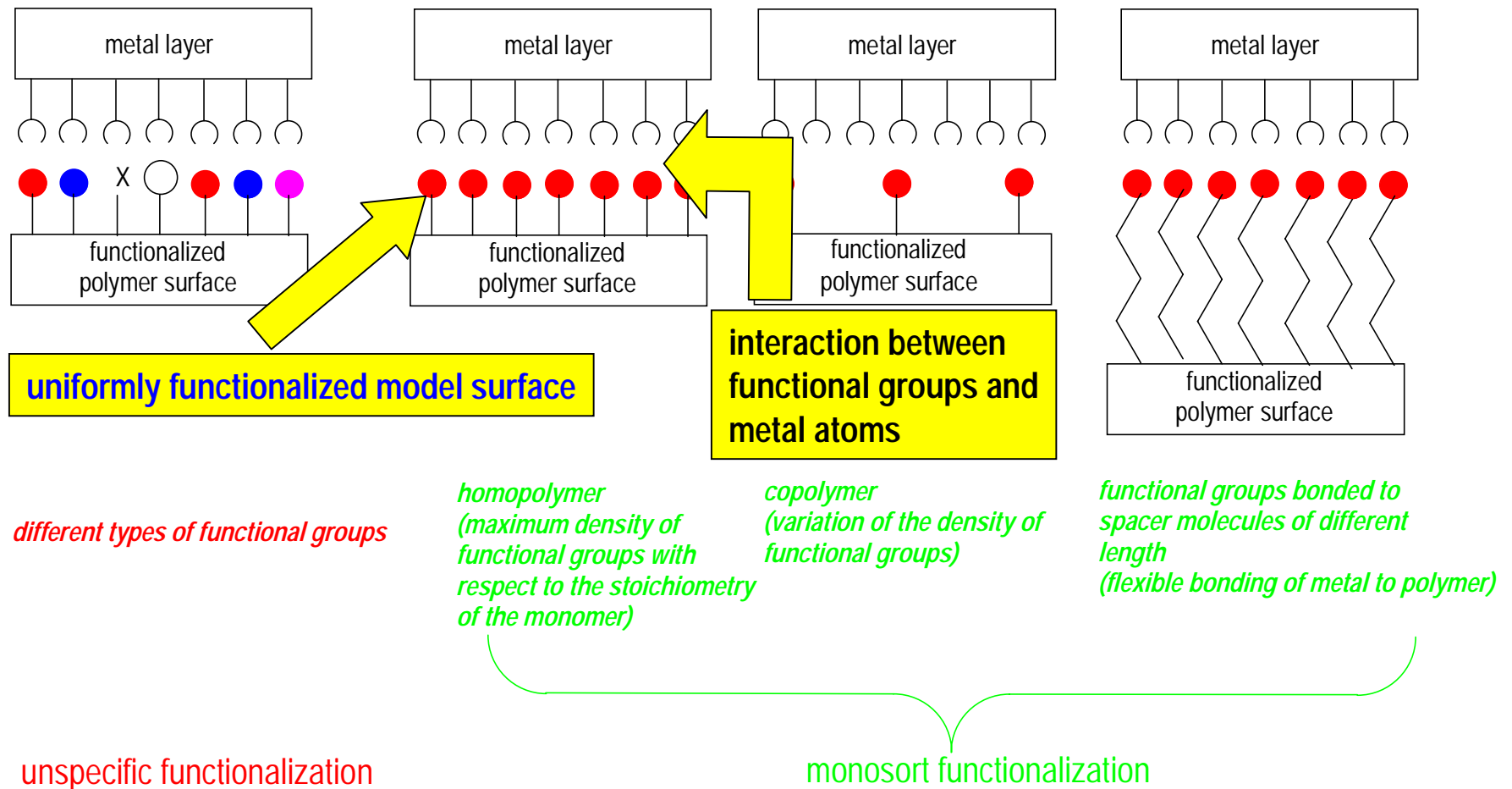
adhesion model



wrapping of nanoparticles for chromatographic phases

Principle

of (chemical) interactions between metal atoms and **MODEL** surfaces with functional groups of different type, concentration and bonding to the polymer



Chemical interactions between metal atoms and functional groups of different type

$$W=N \cdot \omega$$

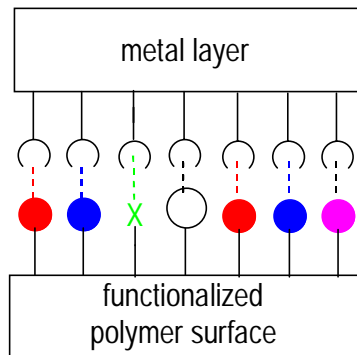
$$N=c \cdot L \cdot A$$

W -Wechselwirkungsenergie, N =Zahl der Gruppen, ω =Wechselwirkungsenergie / Gruppe

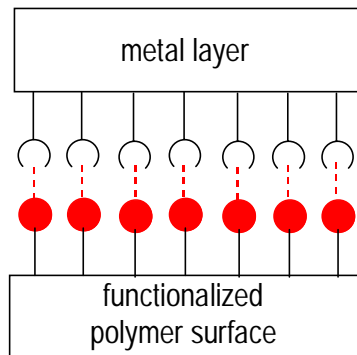
c -molare Konzentration, L -Loschmidtzahl, A -Fläche

$i=1 \dots m$ – Arten der Wechselwirkungen

$$L \cdot \sum_{i=1}^m c_i = c(\text{Funktionalisierungsgrad})$$



$$W=A \cdot L \cdot \sum_{i=1}^m c_i \cdot \omega_i$$



$$W=A \cdot L \cdot \sum c_x \omega_x$$

oxygen plasma (28 O per 100 C):

OH

CHO

COOH

>C=O

C-O-OH

C-O-O•

C-O-C

C-O-O-C

>C=C<

allyl alcohol plasma (31 OH per 100 C):

OH

Functionalization of polymer surfaces in the O_2 plasma

Functionalization of polymer surfaces in the O₂ plasma

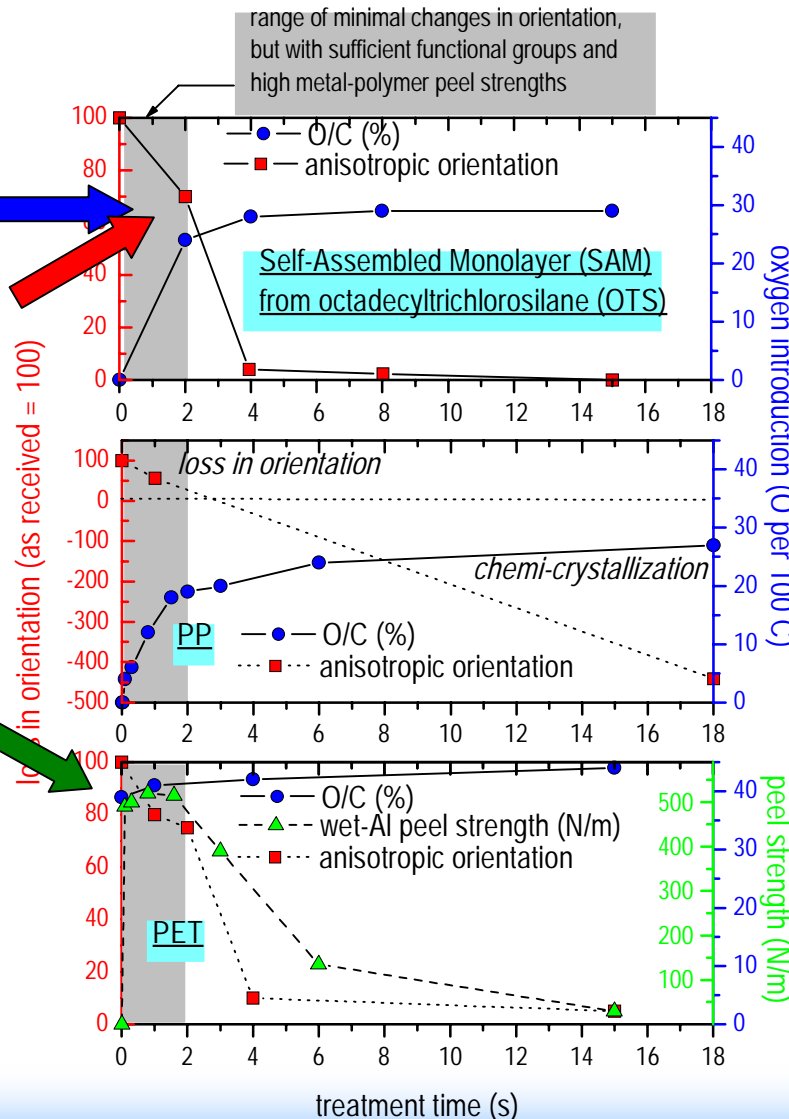
maximum pretreatment – influence on functionalization and supermolecular structure

result:

After 1 - 2 s treatment in the O₂ plasma a **complete surface functionalization** is reached.

Up to 2 s the **original orientation** of macromolecules at the polymer surface is largely **remained** (angle-resolved NEXAFS measurements).

Up to 2 s maximum peel strength in the Al-PET composite were measured.



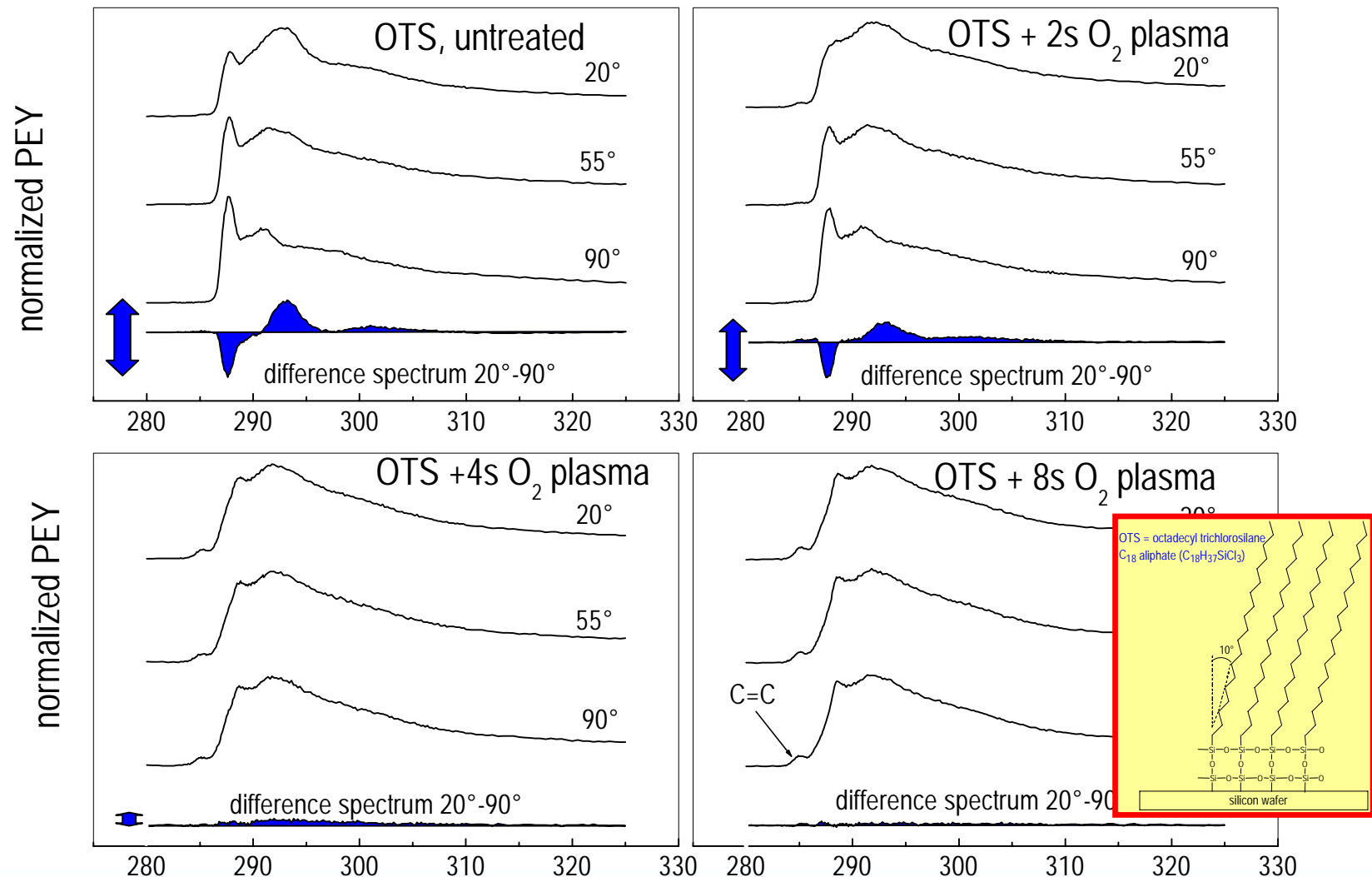
Monomolecular layer of a C₁₈ aliphate at the surface of a Si-wafer (SAM) as model for a polyethylene surface

Polypropylene foil without XPS identifiable additives and surface oxidations

PET-Mylar foil without XPS identifiable additives (only Si) and its thermal evaporation with 300 nm Al

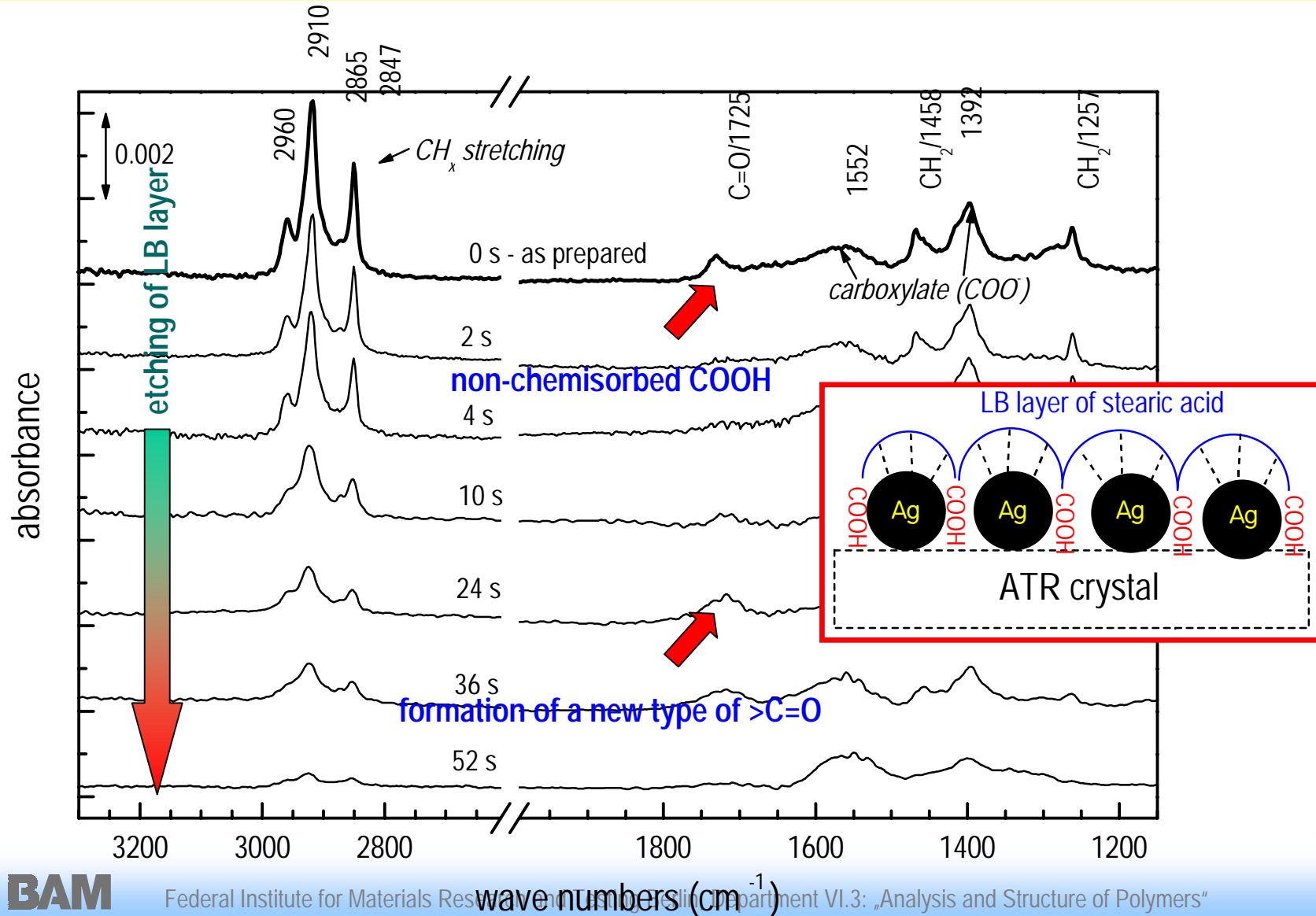
Functionalization of polymer surfaces in the O₂ plasma

maximum pretreatment – loss in supermolecular structure measured by NEXAFS



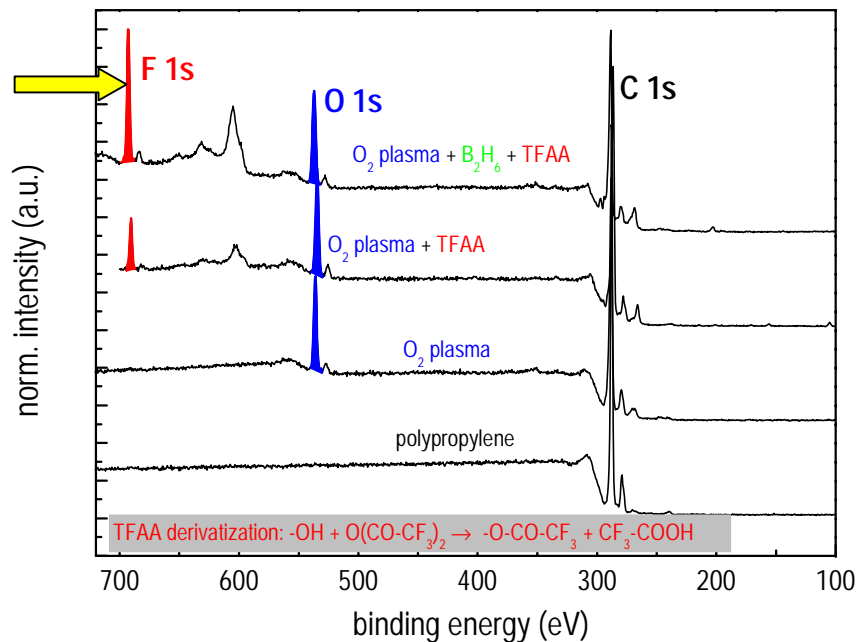
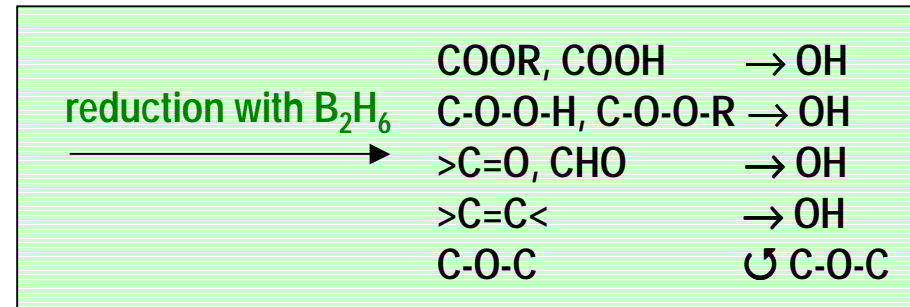
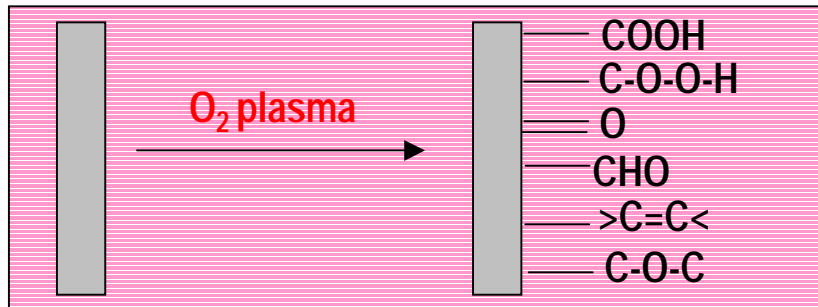
Functionalization of polymer surfaces in the O₂ plasma

functionalization and degradation of LB layer of stearic acid at exposure to oxygen plasma measured by means of SEIRA (Surface-Enhanced IR Absorption)

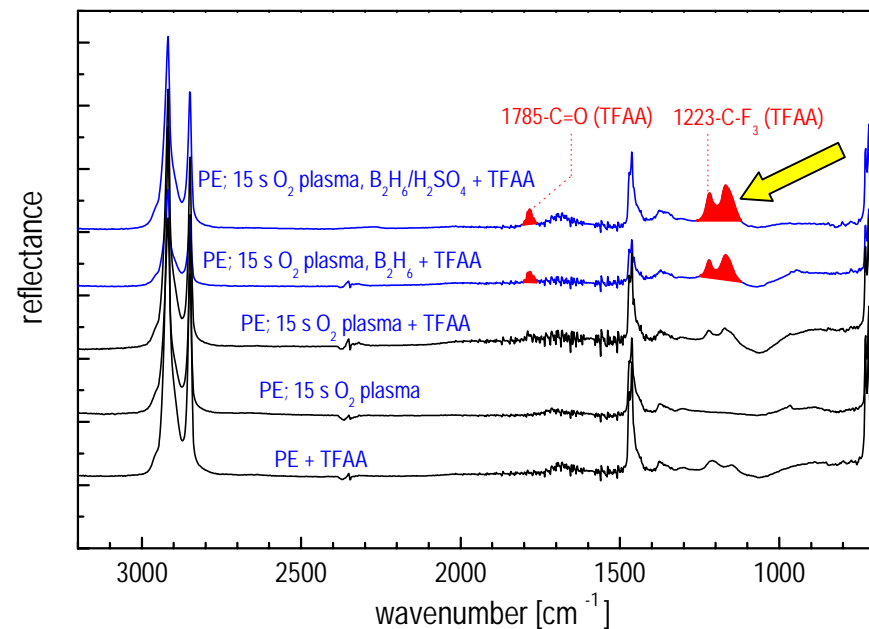


Functionalization of polymer surfaces in the O₂ plasma

combination of plasmachemical functionalization – chemical reduction of O groups to OH



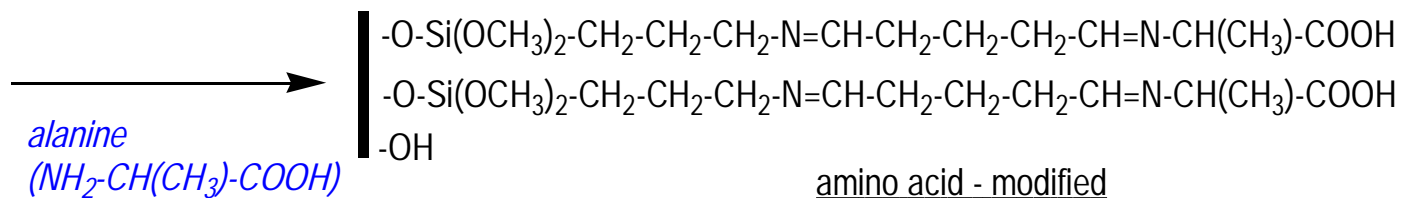
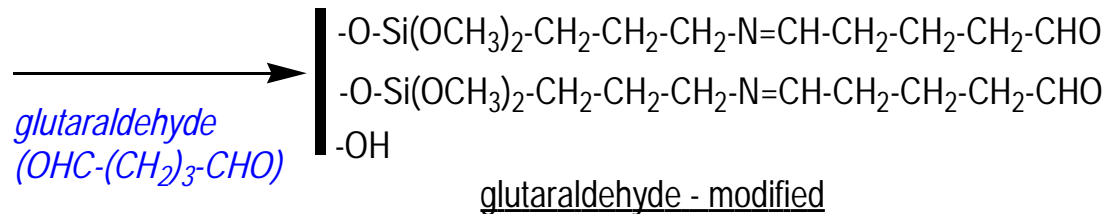
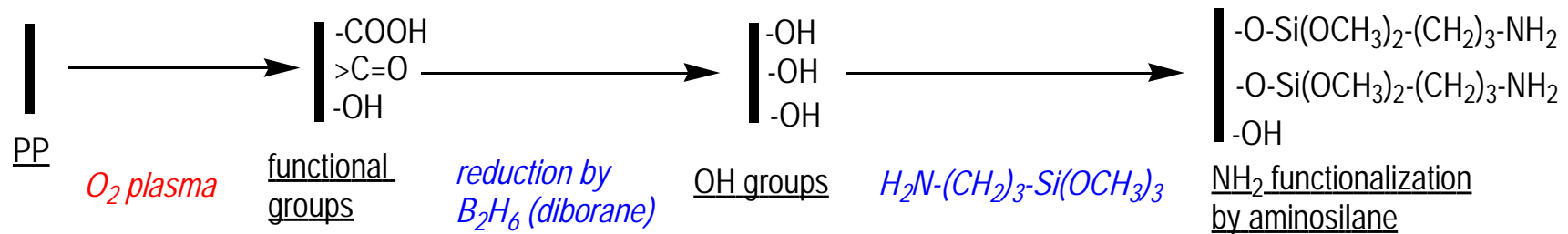
XPS



FTIR

Chemical graft reactions at plasma-introduced OH groups

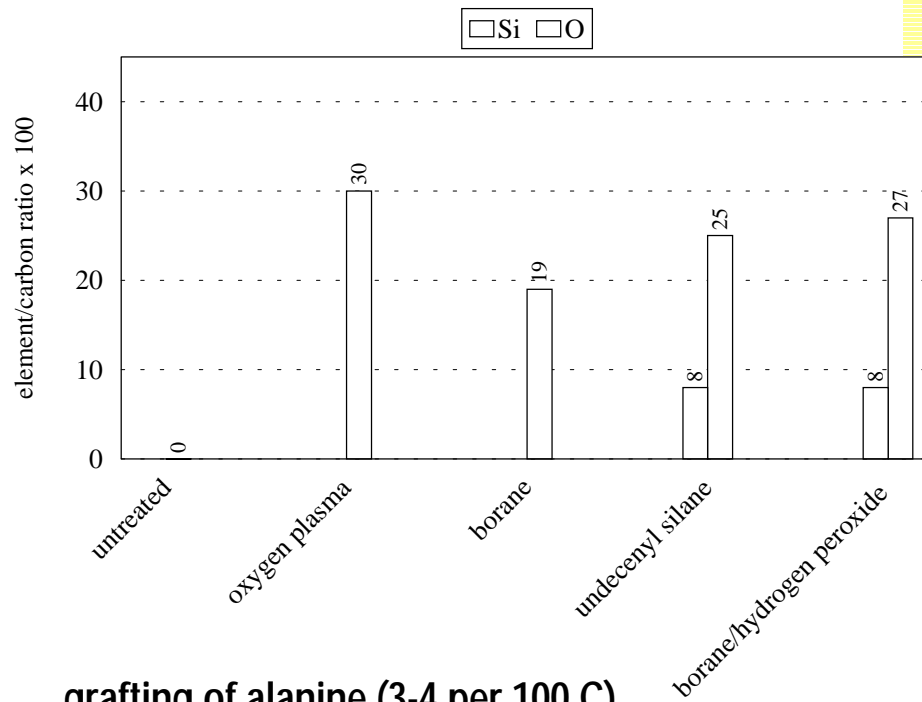
combined process: plasmachemical oxidation in the O₂ plasma and wet-chemical reduction by B₂H₆, LiAlH₄ or vitride™ as well as introduction of spacer or biomolecules



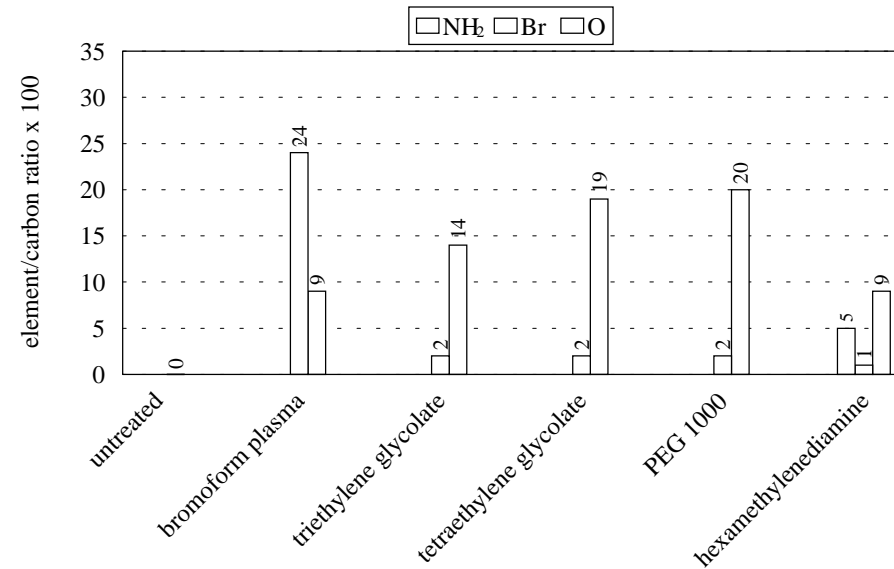
Results of spacer introduction

O_2 plasma + B_2H_6 + spacer

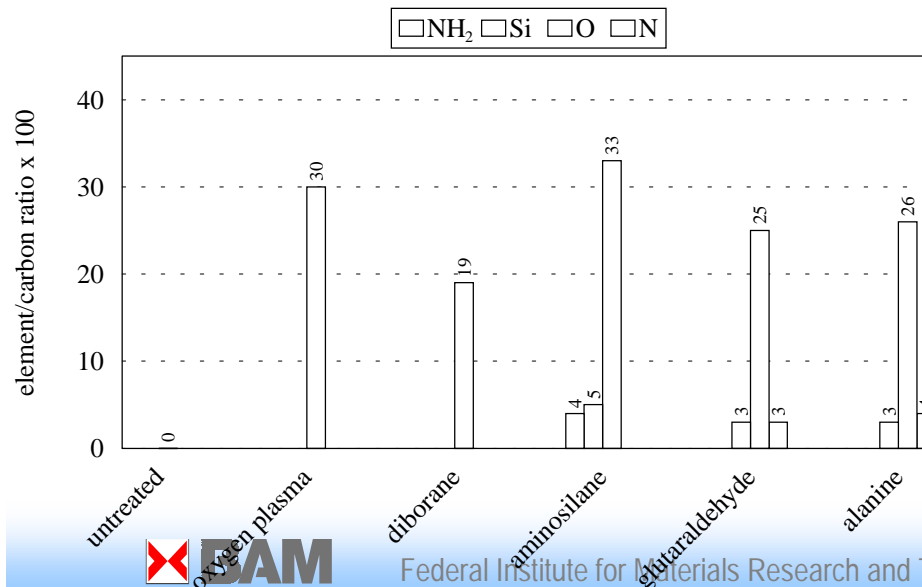
grafting of undecenylsilane (8 per 100 C)



grafting of dioles (5 per 100 C)
and diamines (5 per 100 C)



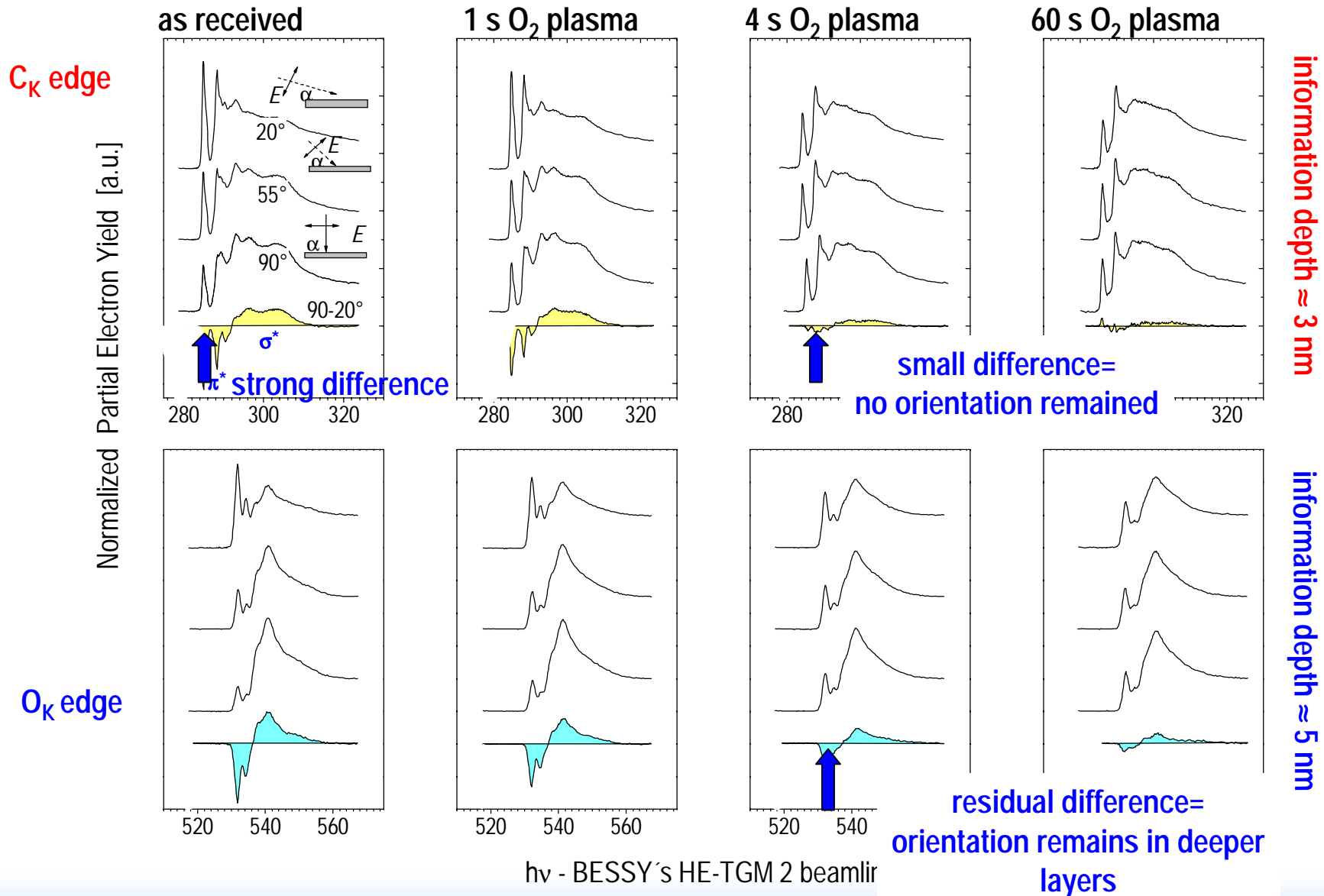
grafting of alanine (3-4 per 100 C)



Degradation behaviour of polymers exposed to the O₂ plasma

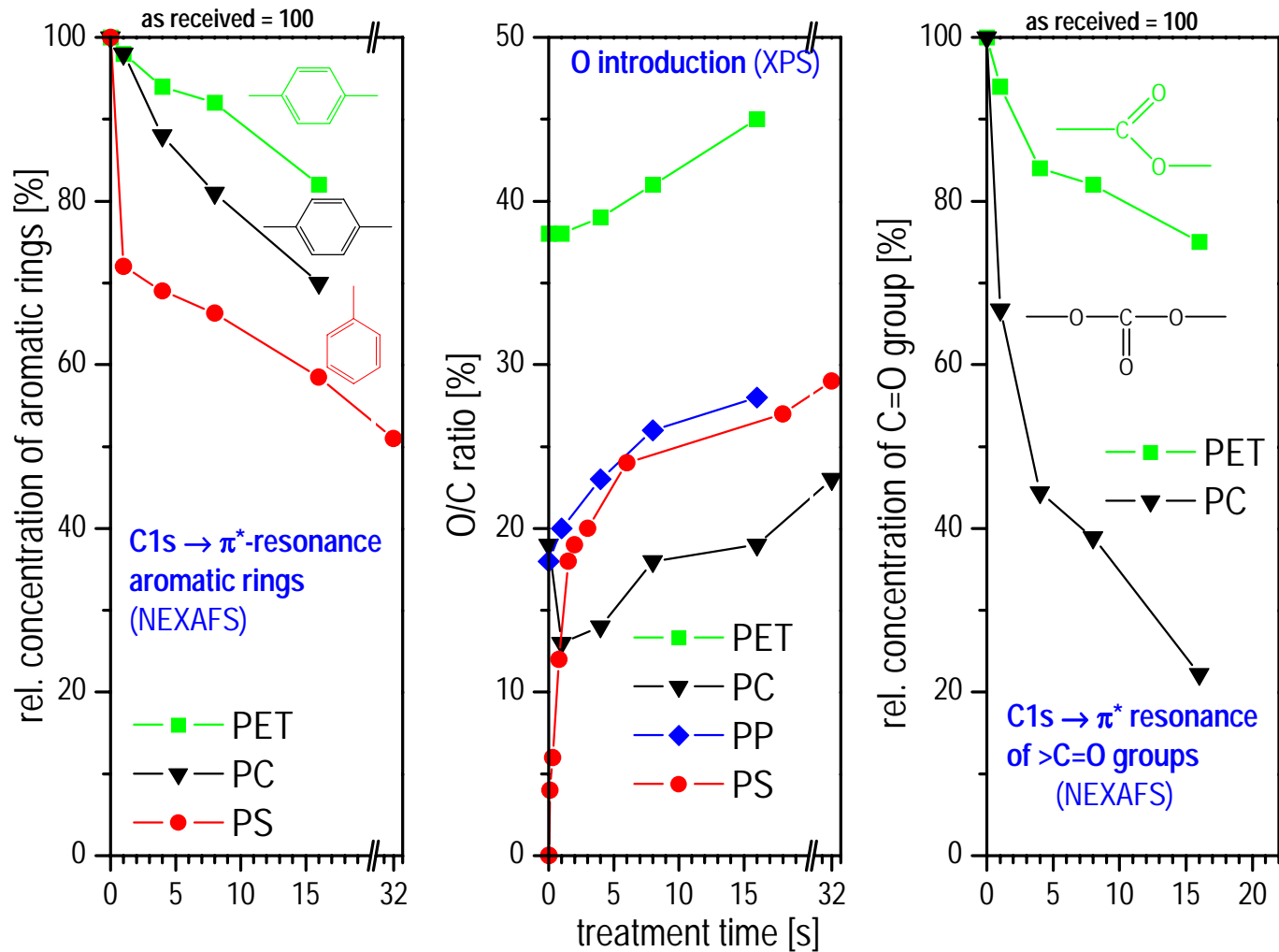
Changes at the surface of PET

NEXAFS results: Loss in orientation and aromaticity



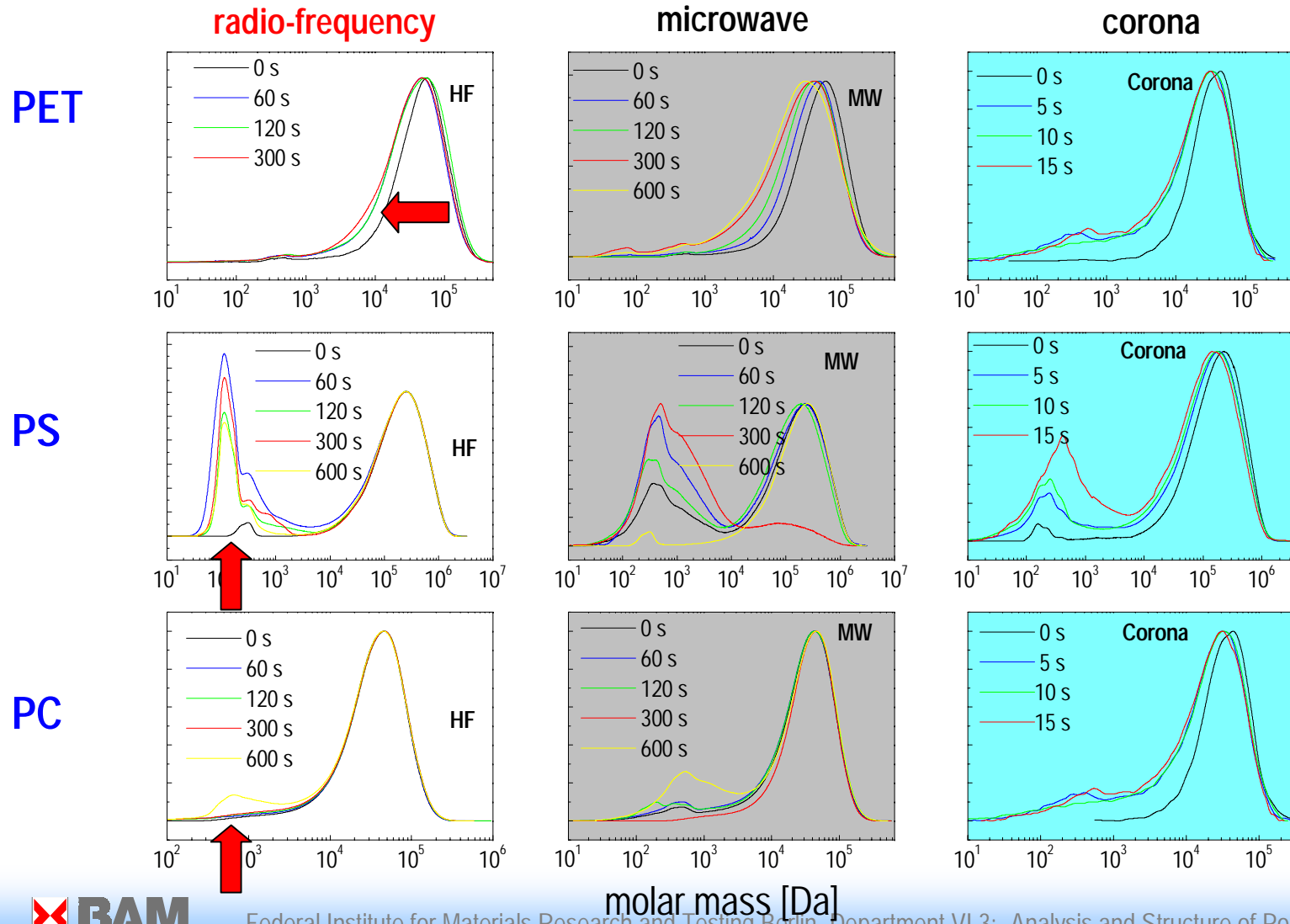
Degradation behaviour of polymers exposed to the O₂ plasma

behaviour of different polymers



Degradation behaviour of polymers exposed to the O₂ plasma or to corona

SEC results

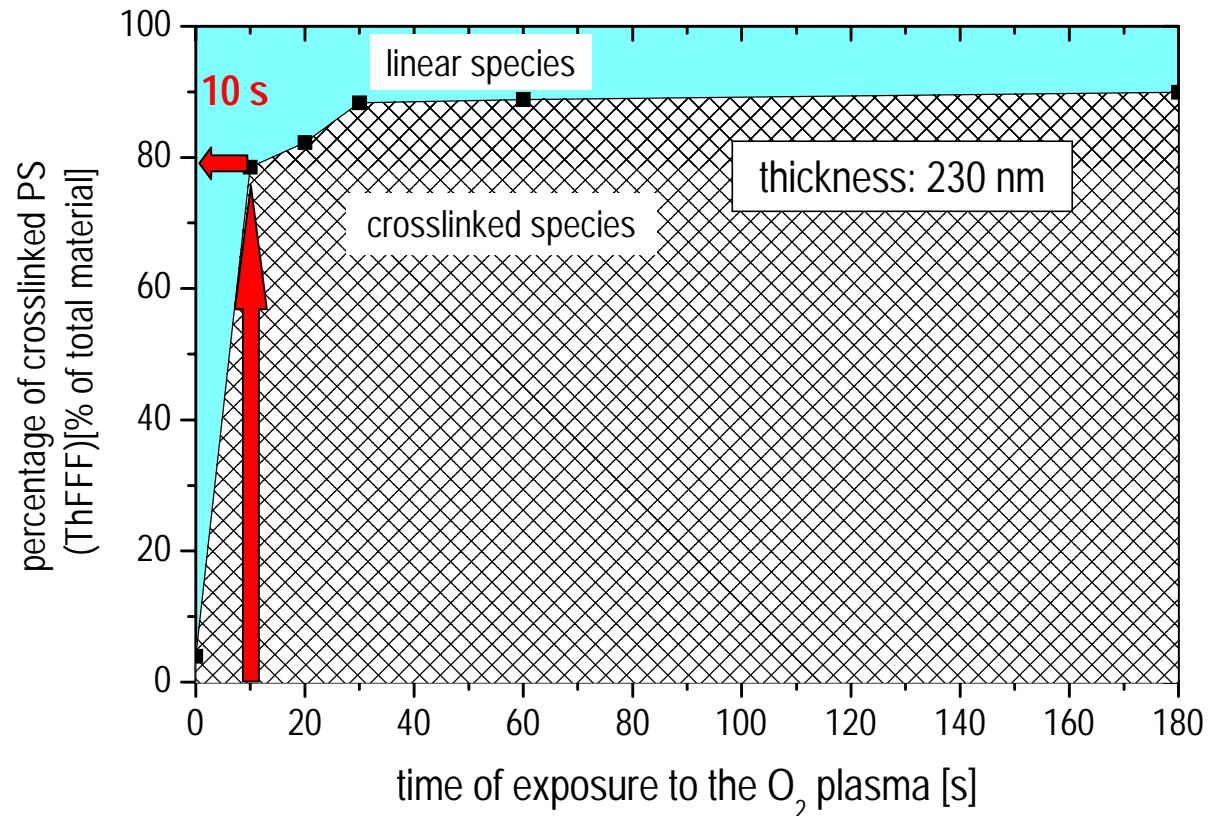


Degradation of PS in the O₂ plasma

crosslinking, Thermal Field Flow Fractionation (ThFFF) results

Results:

After **10 s O₂ plasma** treatment
80% of the **230 nm PS**
layer are (weakly) **crosslinked**.



Thermal Field Flow Fractionation of a thin polystyrene layer for characterisation of the crosslinked part of the polymer (MALLS detection = Multi Angle Laser Light Scattering), which was exposed to the O₂ low-pressure plasma.

Degradation behaviour of polymers exposed to the O₂ plasma MALDI-TOF-MS

Results:

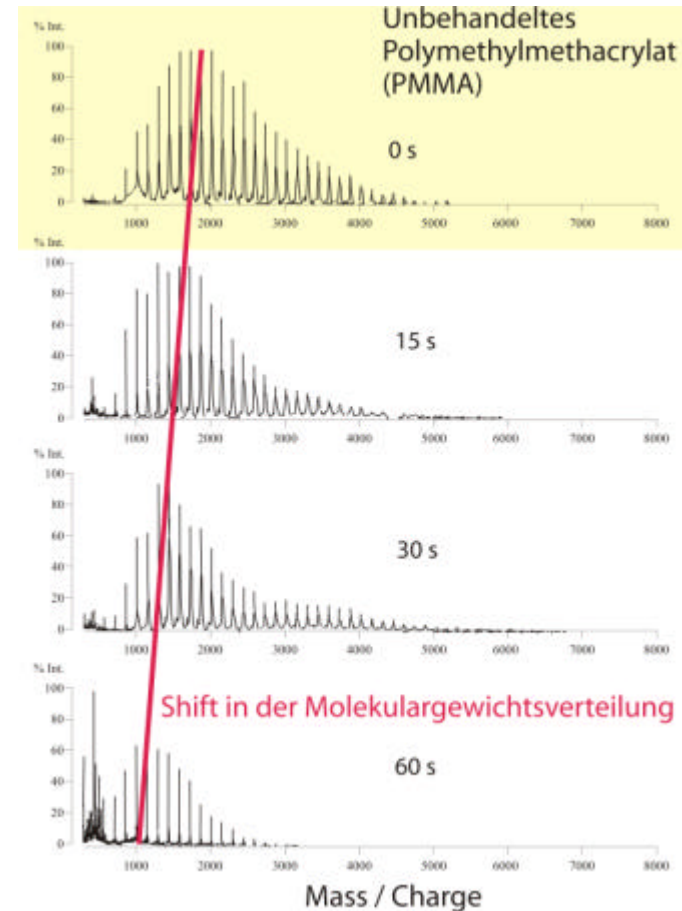
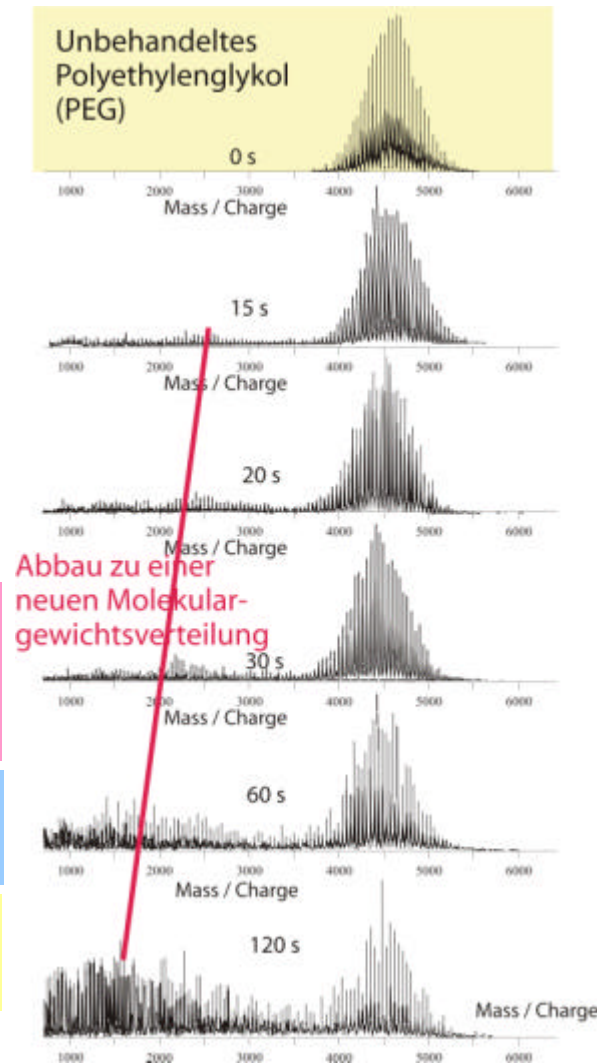
4 different degradation types of polymers at exposure to the O₂ plasma were found:

regular **photo-oxidative degradation** (PET, PC)

depolymerization (PMMA, PS)

random degradation (PEG, PP)

crosslinking (PE, PVC)



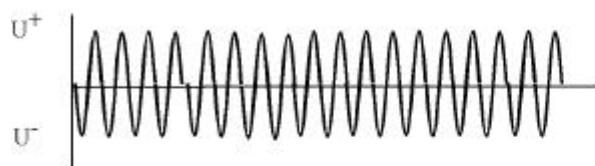
2 examples of molecular weight degradation of polymers exposed to the O₂ plasma

Plasma bromination

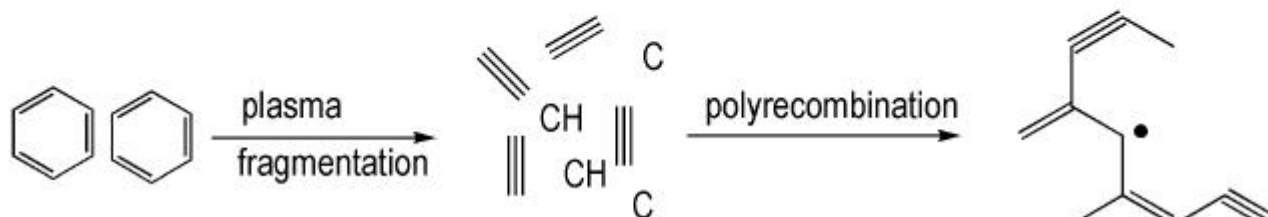
Pulsed plasma polymer layers

Principle of pulsed plasma technique

CONTINUOUS WAVE PLASMA

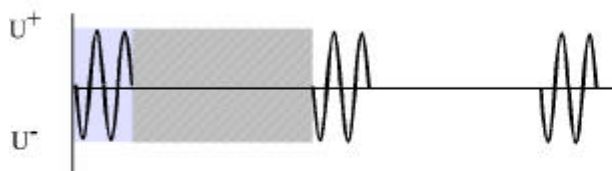


plasmainitiated fragmentation and polyrecombination ("atomic polymerization")

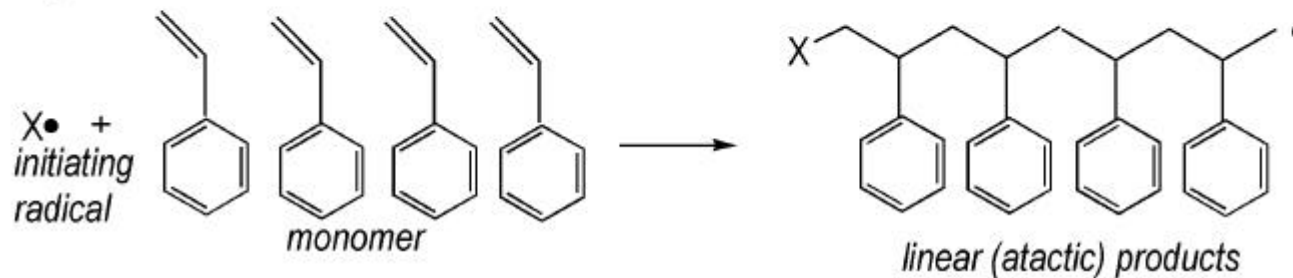


highly crosslinked, unsaturated and radical-rich product of irregular structure

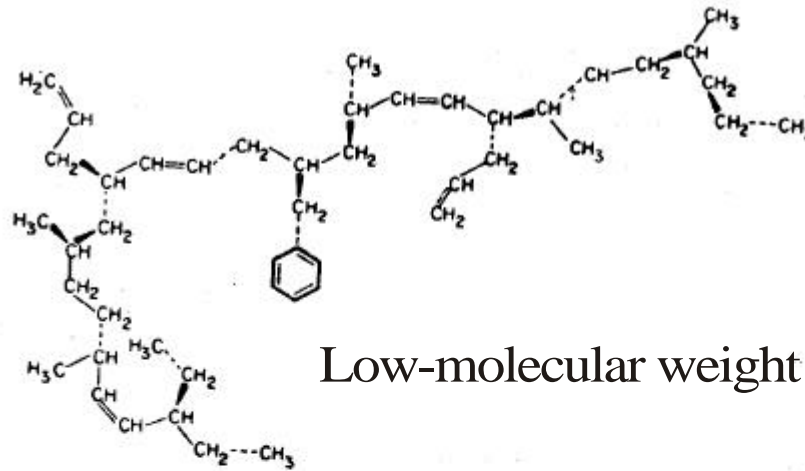
PULSED PLASMA



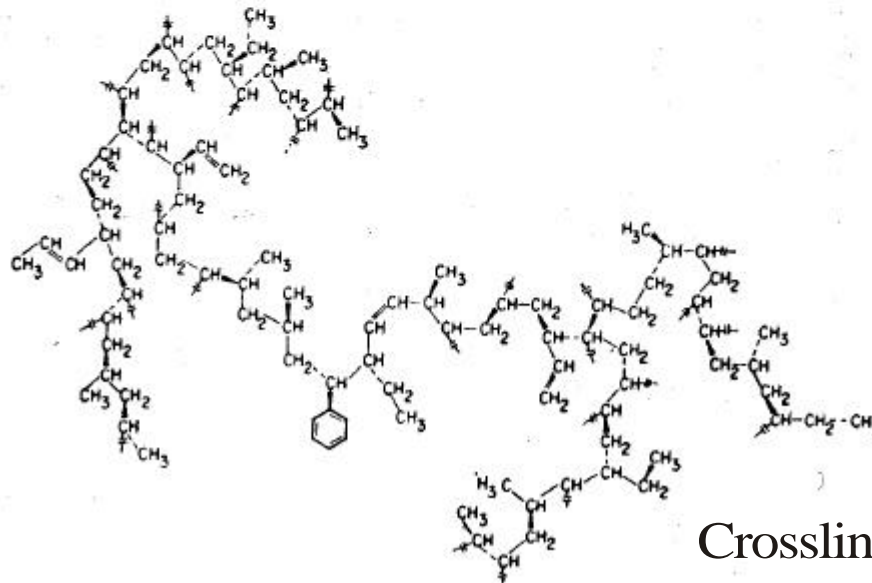
plasma activation + radical gasphase polymerization



Polymer produced in the continuous-wave plasma



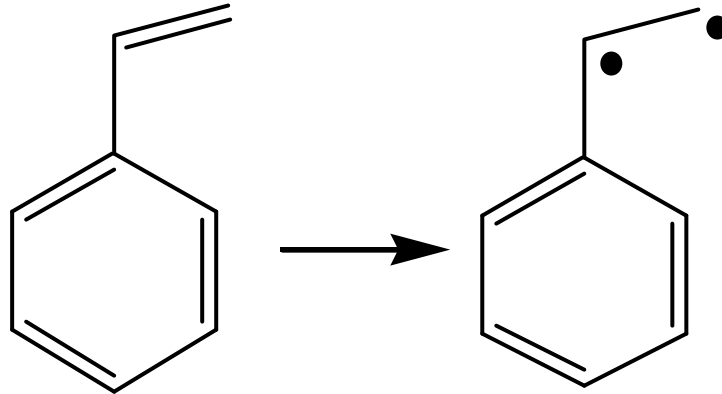
Low-molecular weight product



Crosslinked product

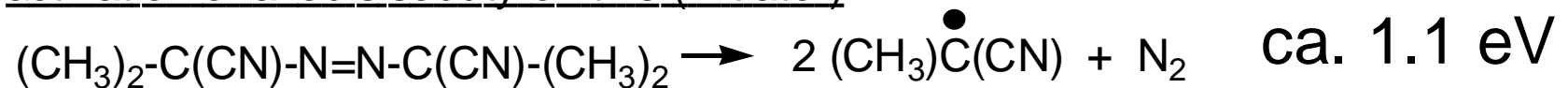
Chemical (radical) polymerization

activation of styrene



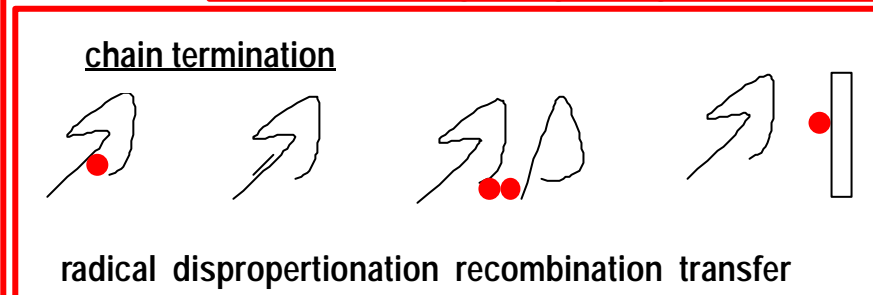
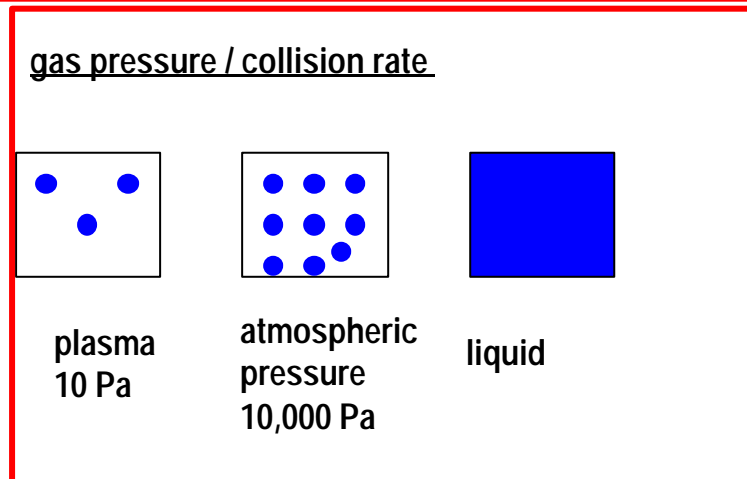
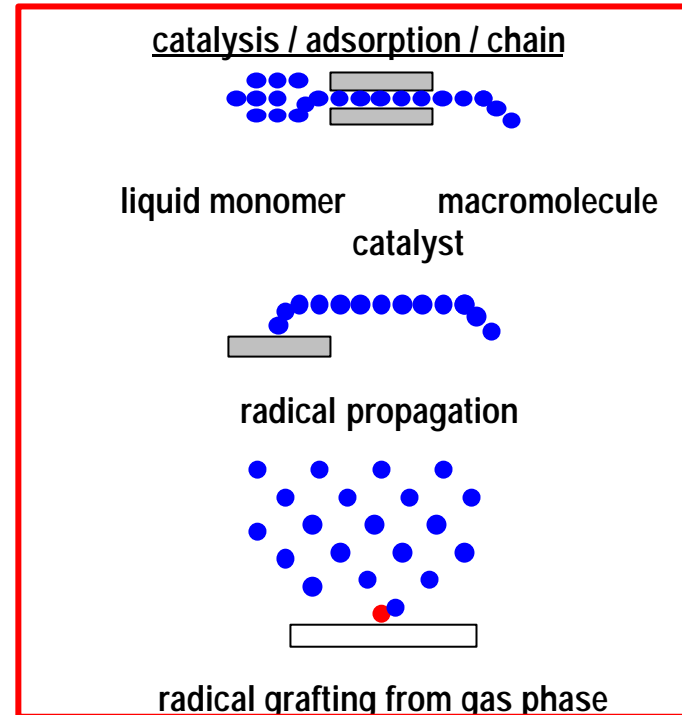
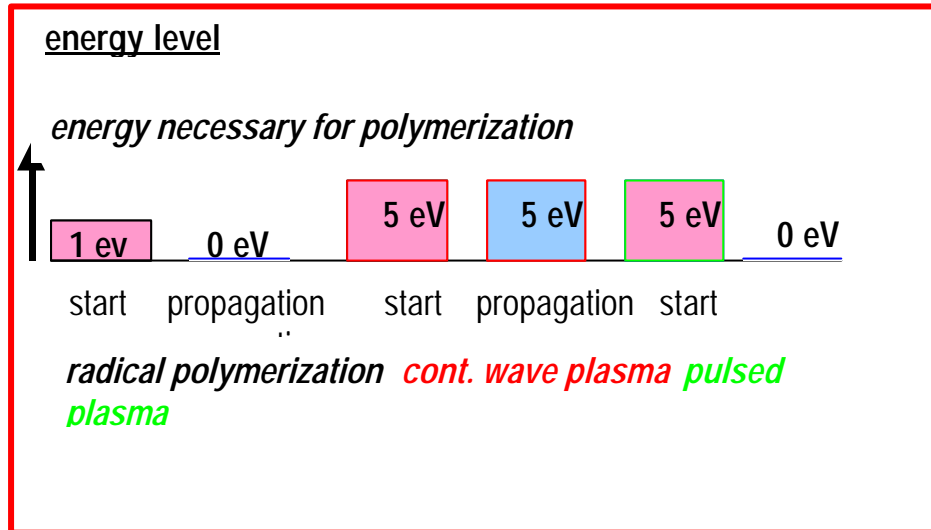
ca. 1 eV

activation of azobisisobutyronitrile (initiator)



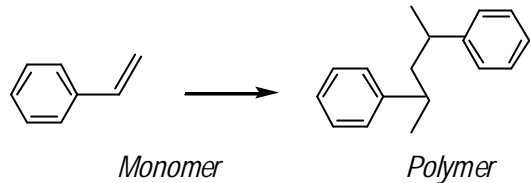
- For a radical chain propagation one initiating step is needed
- Vinyl or acrylic monomers are well-suited for a radical chain polymerization
- Using AIBN as initiator or activating styrene directly about 1 eV is consumed for initiating the chain
- After initiation the chain propagation does not need additional energy, reaction heat is form (exothermal reaction)

Comparison classic and plasma polymerization



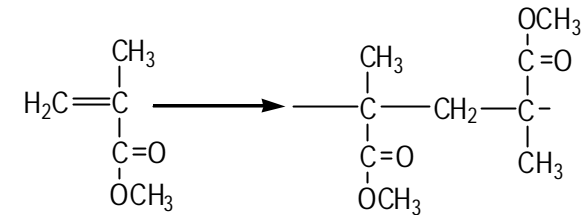
Monomers suited for chemical (radical) polymerization

well qualified (vinyl, acrylic monomers)



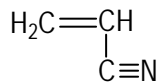
styrene

*well-suited, low activation energy,
molecule is stable in the plasma,
intermediate styryl radical is resonance
stabilized*



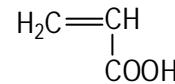
methylmethacrylate

*well-suited, low activation energy,
monomer molecule has tendency to fragment
at the ester group in the plasma*



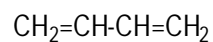
acrylonitrile

*well-suited
tendency of oxygen uptake
and reaction at the CN group*



acrylic acid

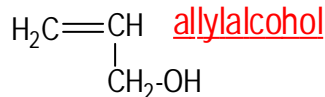
*well-suited
decarboxylation/decarbonylation
of COOH*



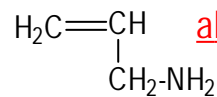
butadiene

suited, tendency of crosslinking

moderately qualified

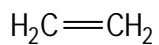


allyl alcohol



allylamine

*allyl monomers has low reactivity,
radical intermediate tends to
resonance stabilization and
therefore, to chain termination*



ethylene

low reactivity, tends to branching and crosslinking

unqualified

aromatics

benzene

toluene

aliphatics

n-hexane

cyclohexane

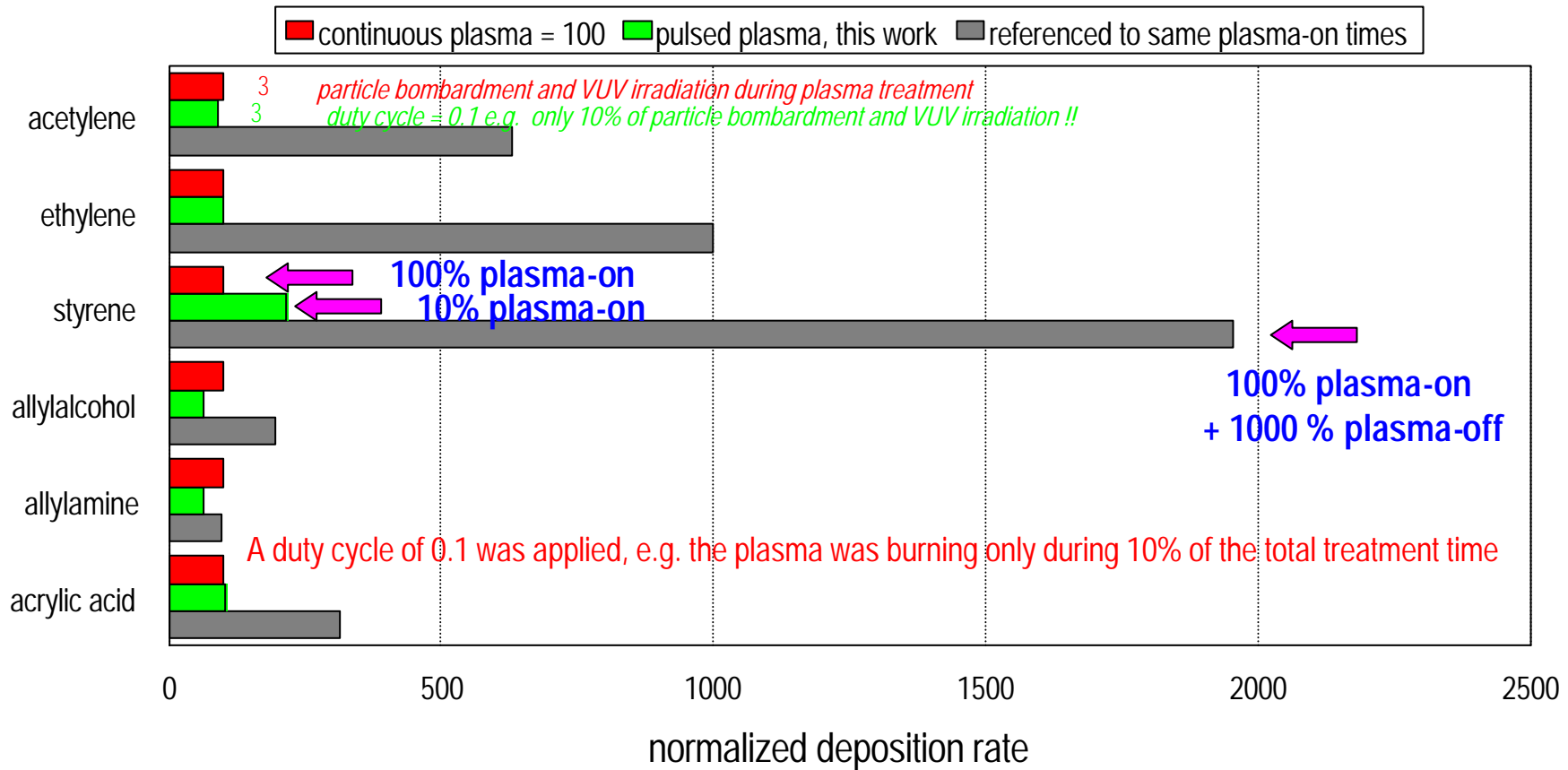
DACH

ethers, ketones, aldehydes

Pulsed plasma polymerization of styrene as model reaction

Pulsed plasma polymerization

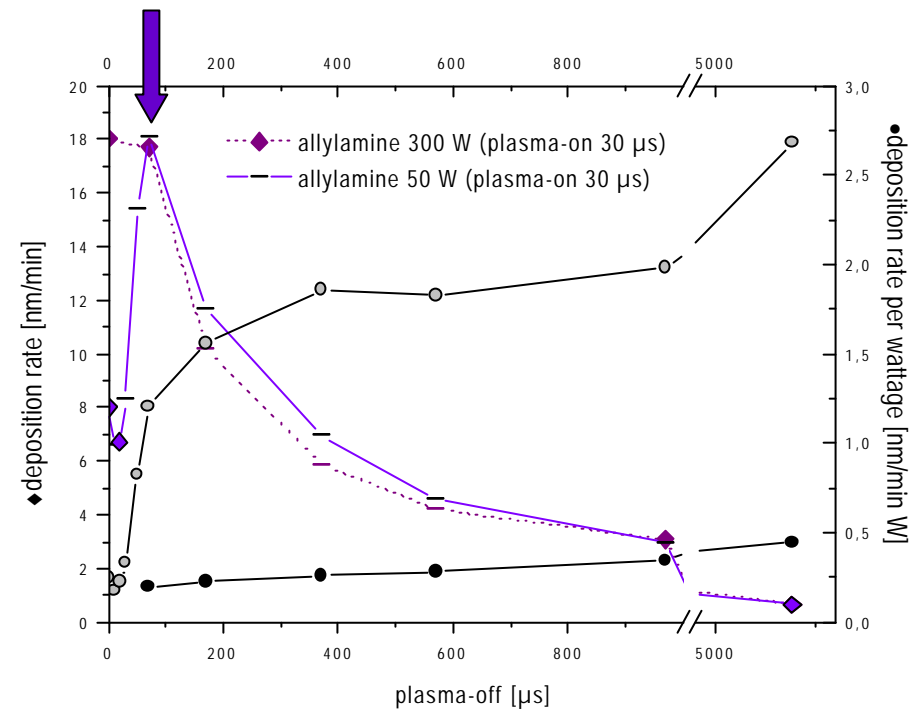
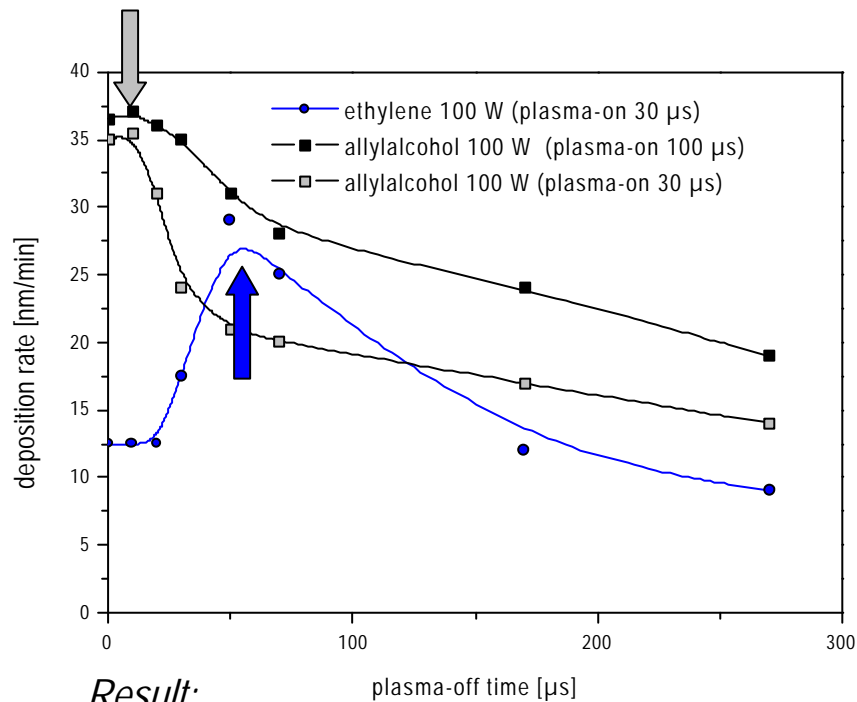
The chemical contribution to the pulsed plasma polymer formation is obviously by comparing the deposition rates in the continuous and in the pulsed plasma. The effective plasma-on time in the pulsed plasma was 10% of that of the cw plasma, however, the deposition rates are similar.



G-values of pulsed plasma polymerization are ca. 2500 and the mean polymerization degree is 25 indicating regular radical polymerization.

Pulsed plasma polymerization

dependence of the deposition rate on plasma-off time at given pulse duration (30 μs)



Result:

The *ethylene* pulsed plasma polymerization shows a **maximum of the deposition rate** at plasma-on / plasma-off:

30 μs -on / 60 μs -off (1:2)

allyl alcohol

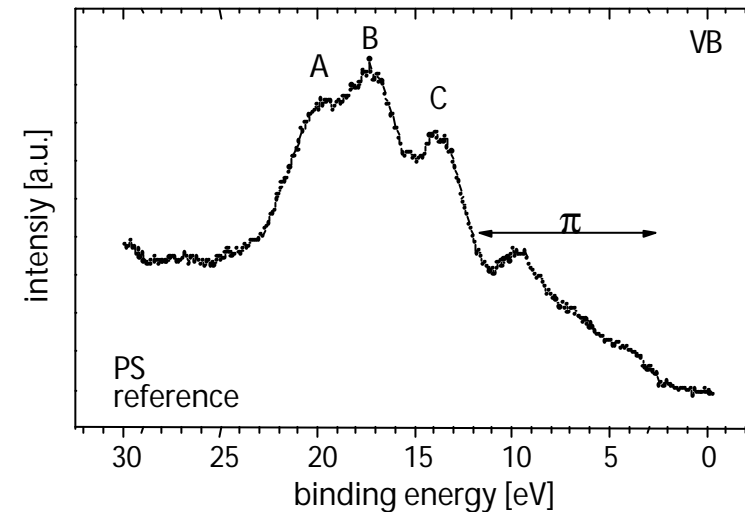
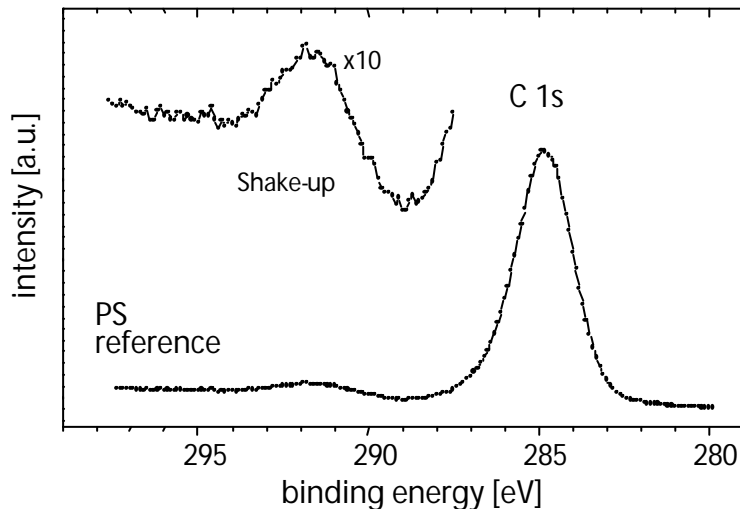
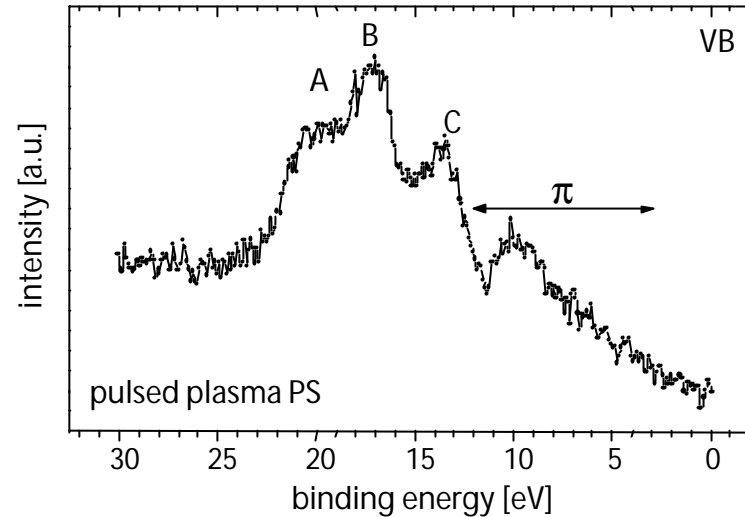
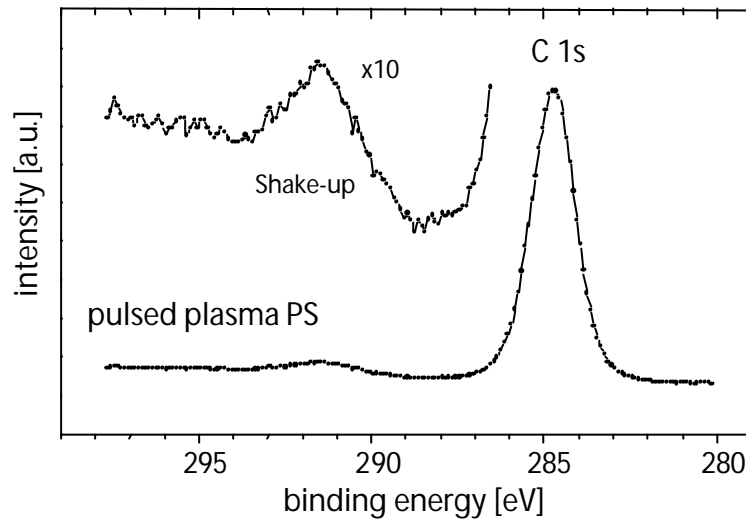
30 μs -on / 20 μs -off (1:0.7)

allylamine

30 μs -on / 75 μs -off (1:3)

ethylene

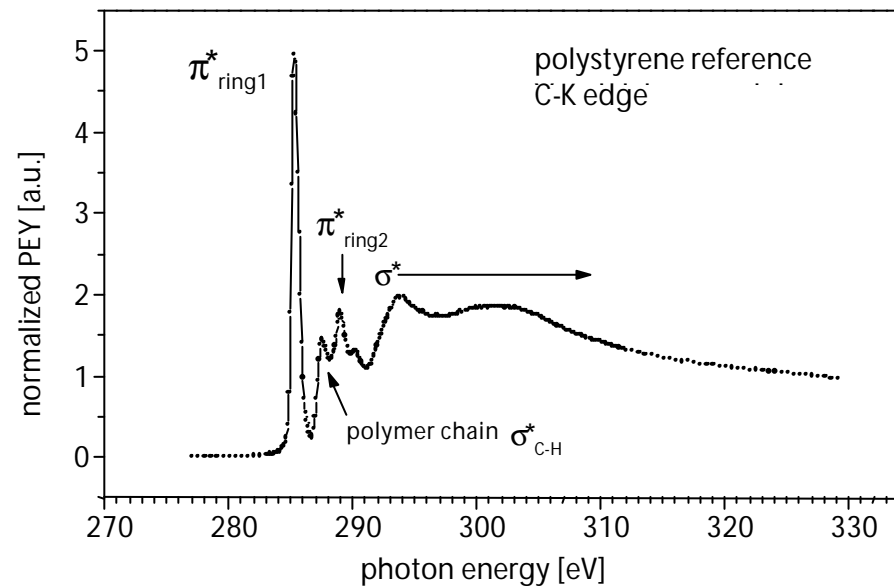
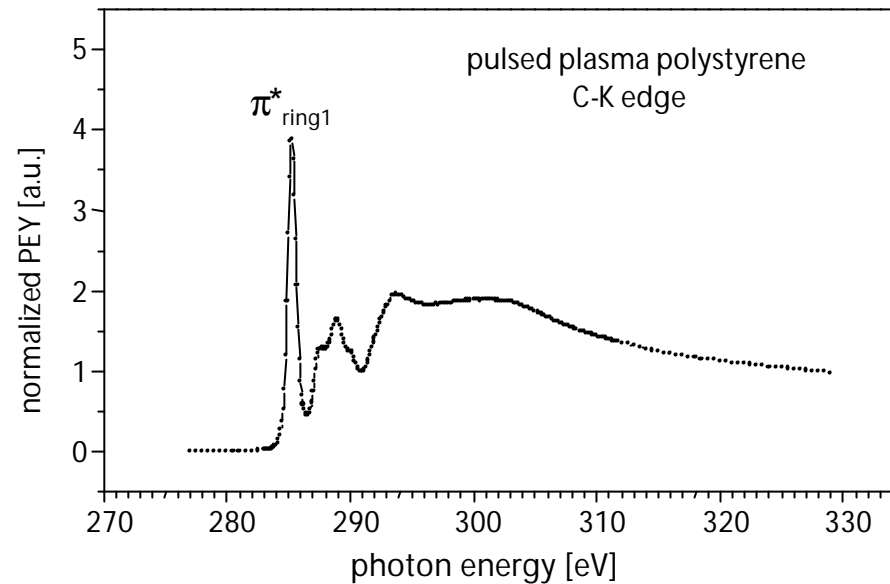
Shake-up satellite in the XPS C1s region and valence band spectra of pulsed plasma polymerized polystyrene



Result: identical C1s and valence band spectra of pulsed plasma polystyrene and reference PS

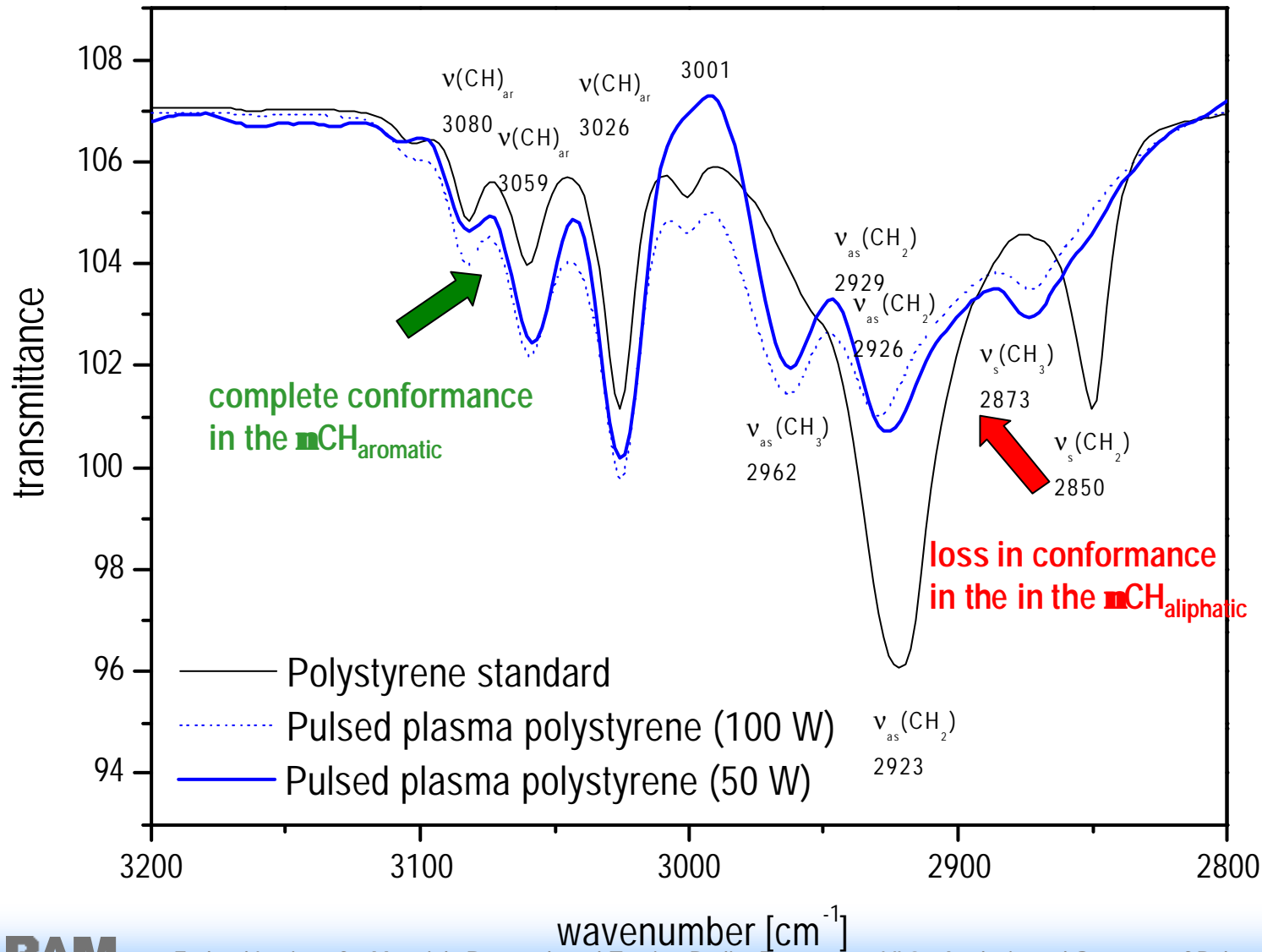
NEXAFS (near-edge X-ray absorption fine structure) spectra of pulsed plasma PS and reference PS

Result: comparable NEXAFS spectra of pulsed plasma polystyrene and reference PS



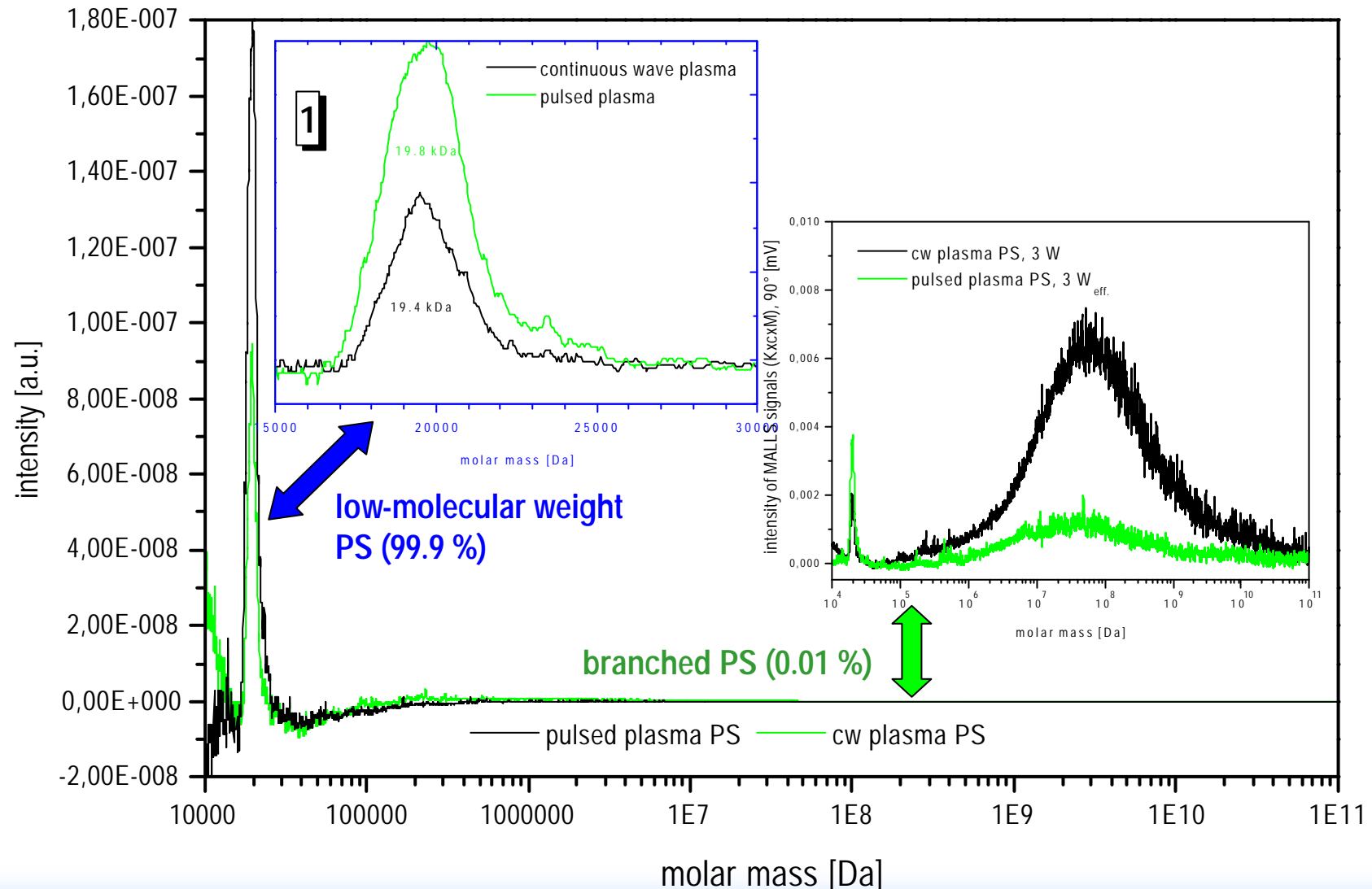
FTIR spectra of pulsed plasma PS in the region of νCH

Result: The aromatic rings remains intact, however, the polymer backbone is changed



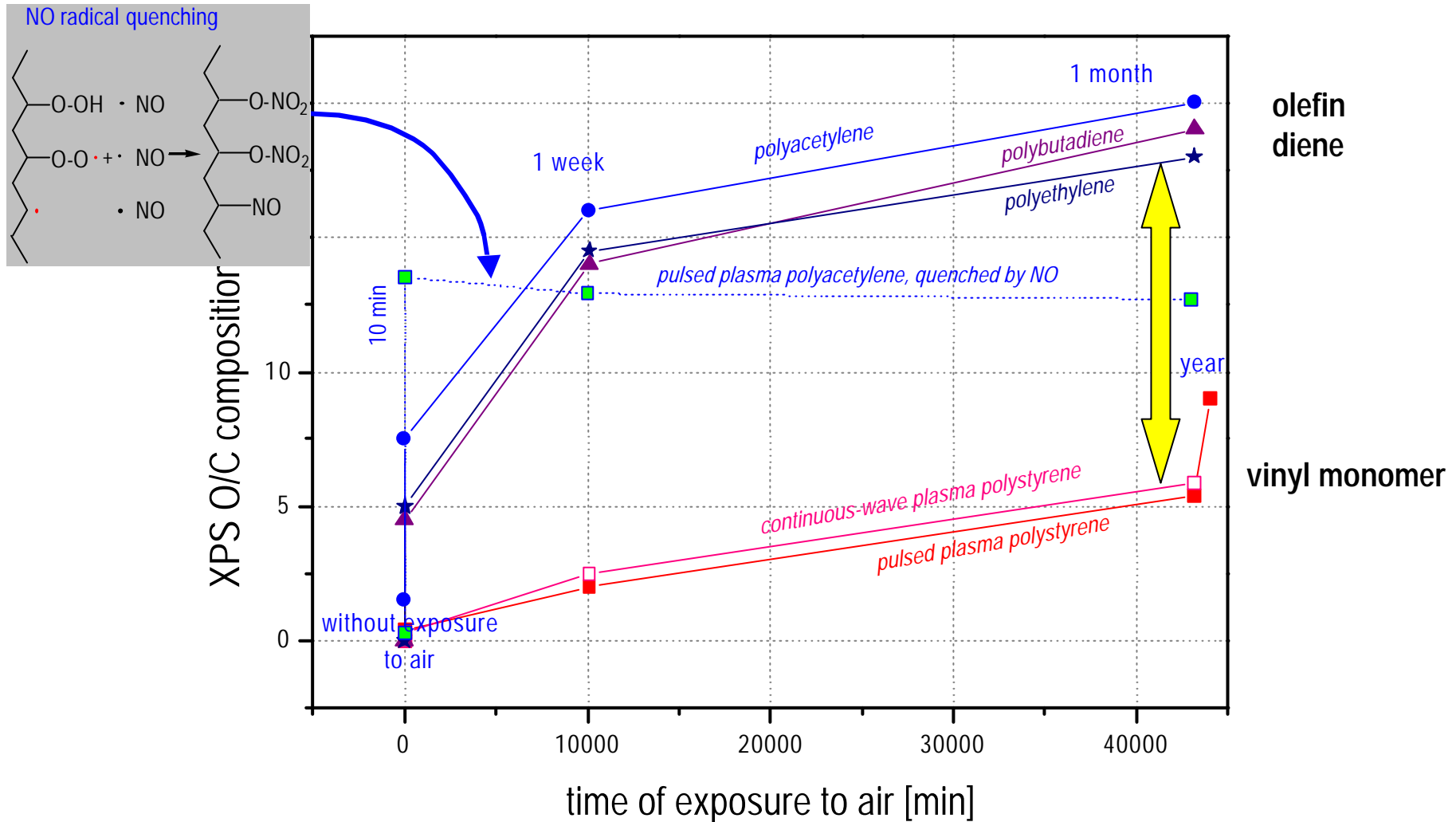
Pulsed plasma polymerisation of styrene

characterised by the molar mass and its distribution measured by Thermal Field Flow Fractionation



Stability of pulsed plasma polymers

Oxygen uptake of plasma polymer layers after exposure to air



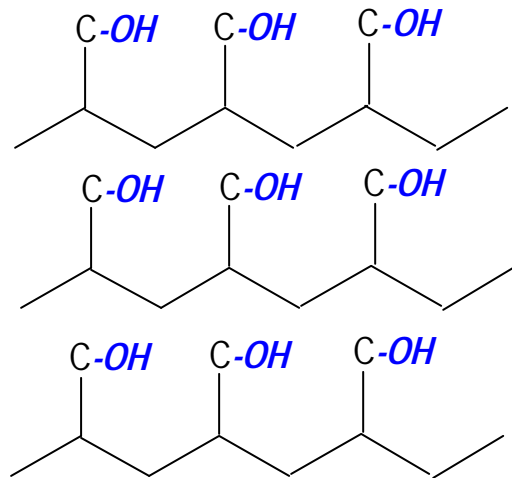
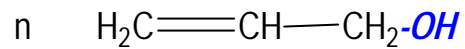
Result: cw and ppPS show a similar good stability at exposure to ambient air. In contrast the pulsed plasma acetylene, butadiene and ethylene pick up high concentrations of oxygen. **NO quenching stabilized** the layers. Information depth: **5-10 nm.**

Functional groups carrying plasma polymers

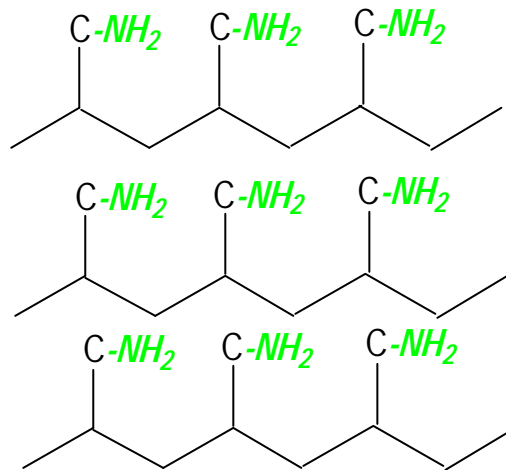
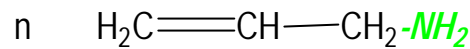
Homopolymerisation

Polymer (substrate) surface functionalization by pulsed plasma polymerization of functional groups bearing monomers to thin layers of (relatively) defined chemical composition and structure

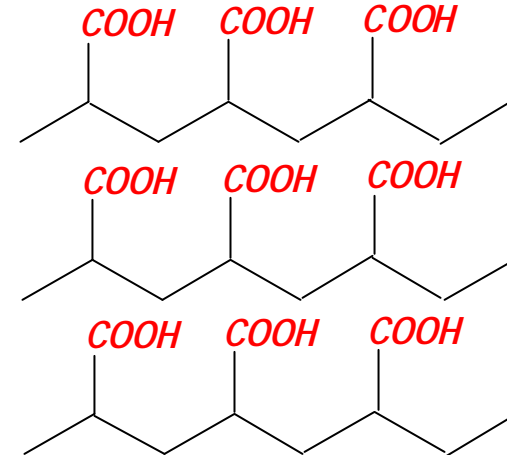
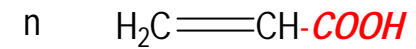
allyl alcohol



allylamine

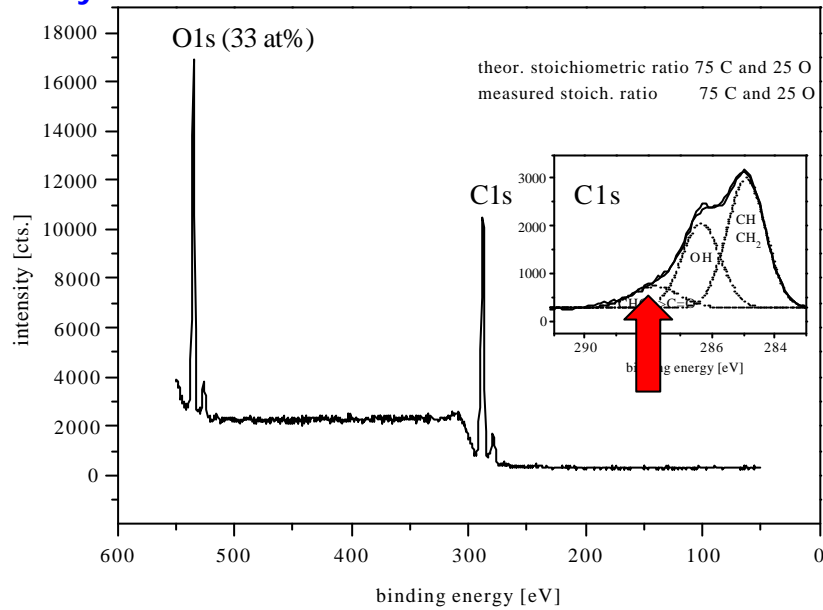


acrylic acid

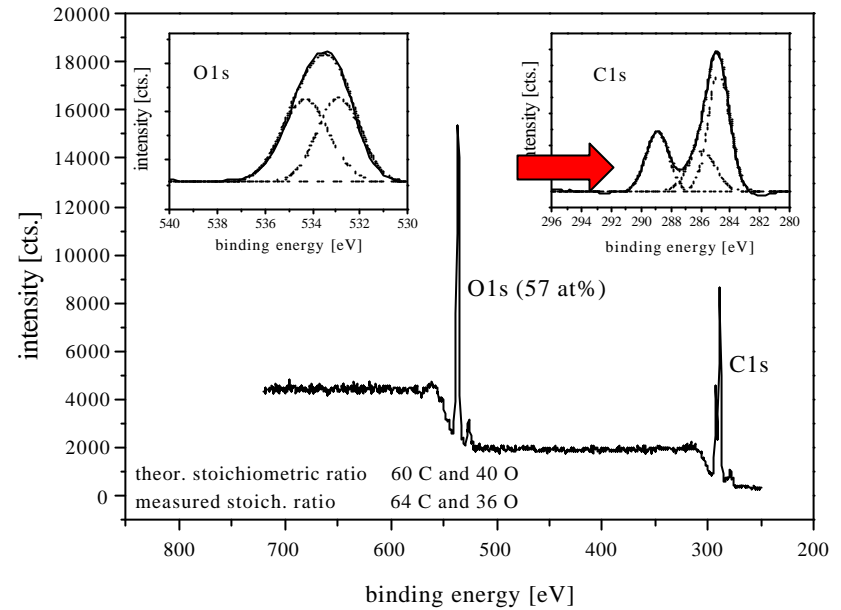


Pulsed plasma homopolymers

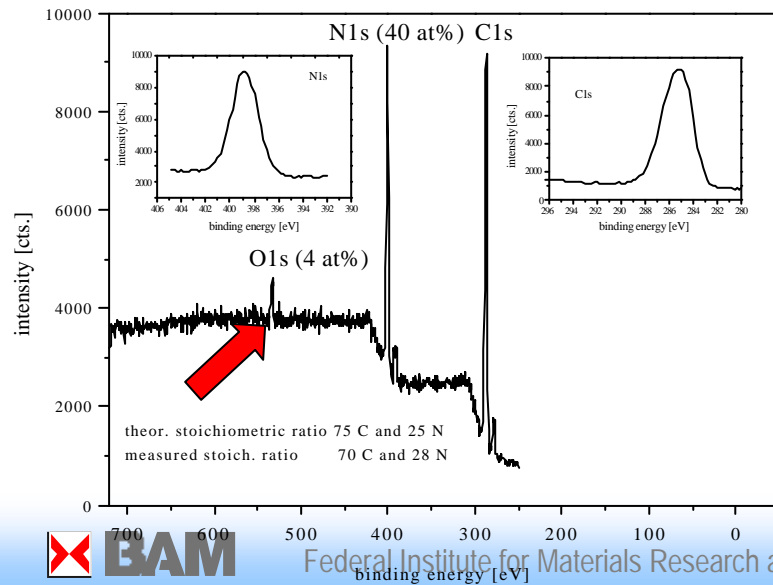
allyl alcohol OH



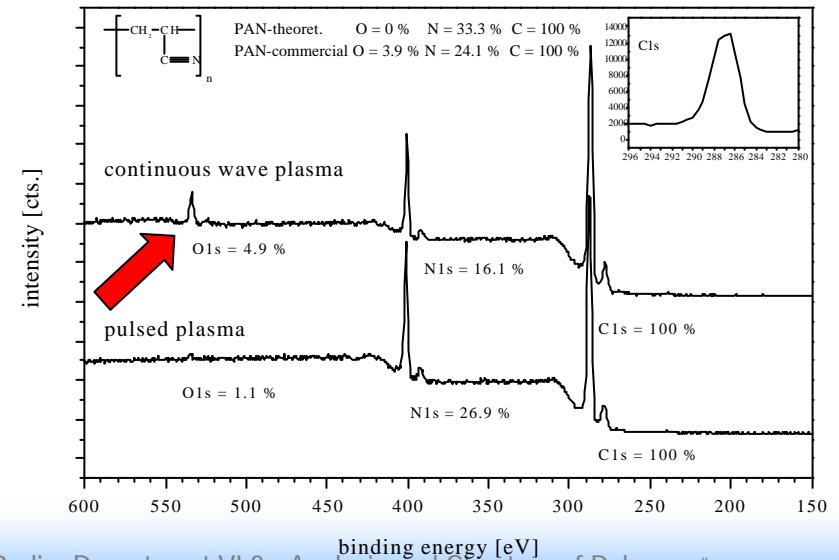
acrylic acid COOH



allylamine NH₂



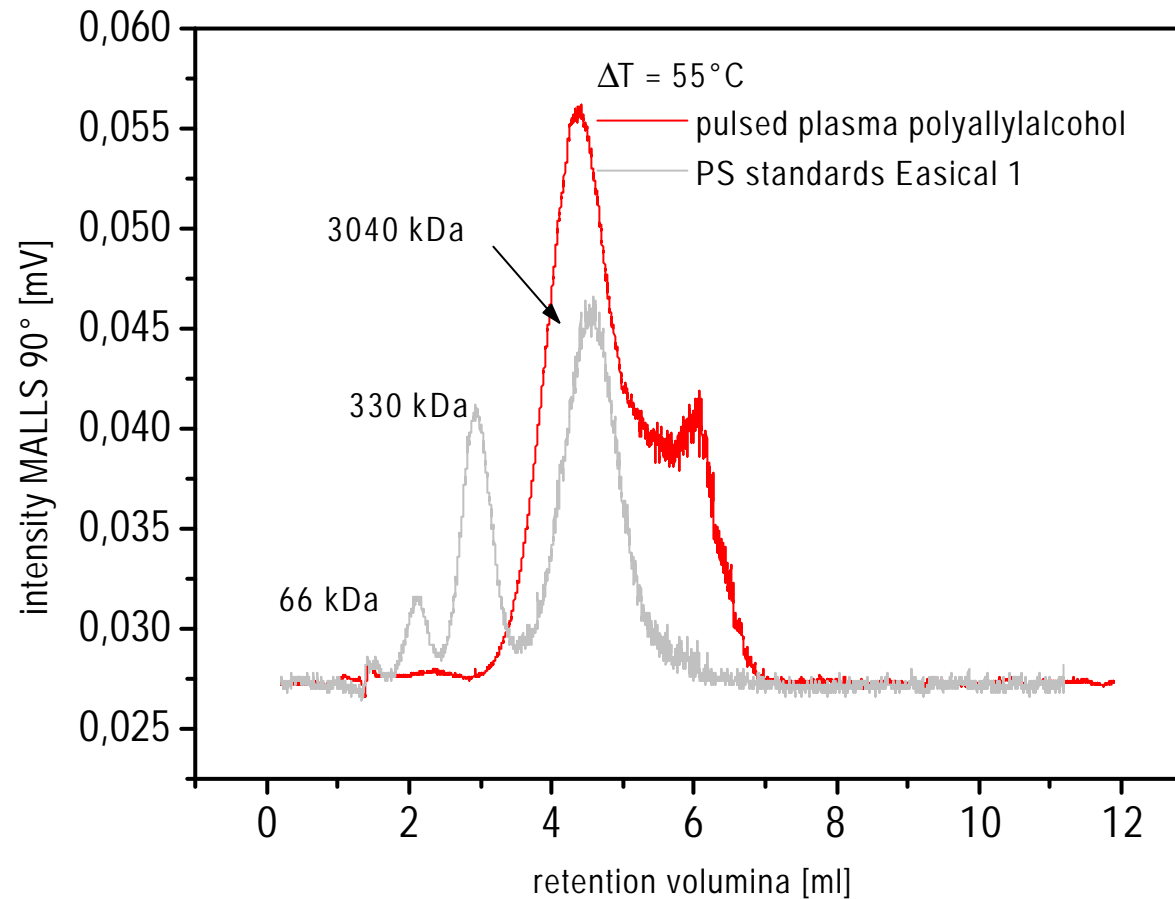
acrylonitrile CN



Structure of pulsed plasma homopolymers

ThFFF of pulsed plasma-polyallylcohol

Result:
pulsed plasma
polyallylcohol shows a low
or moderate molecular
weight



Homopolymerization

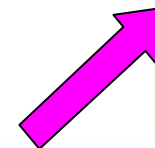
Measured yields of functional groups at polymer surfaces using the pulsed plasma polymerization of functional groups carrying monomers

Monomer	XPS measured elemental composition (%)	C1s peak fitting(%)	Derivatization results			
			Retention of X (%)	X per nm ²	pmol per mm ²	X per 100C limit 33 gr.
Acrylic acid	90 (O)	80	73	1.5	2.2	≈ 24 COOH
Allylalcohol	100 (O)	75	95	1.8	2.9	≈ 31 OH
Allylamine	>100 (N)	100	55	1.1	1.9	≈ 18 NH ₂

yield



number



Homopolymerization

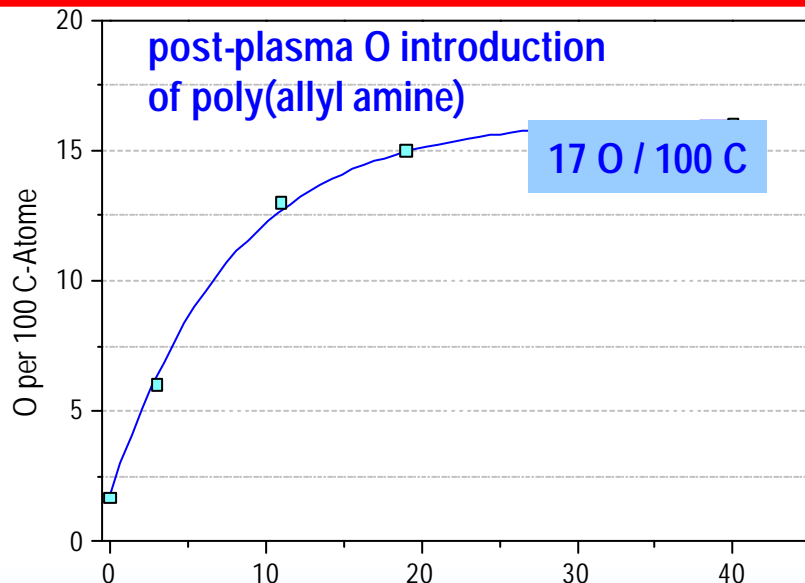
Ageing of functional groups-carrying plasma polymers

stability of pulsed plasma polymers during storage

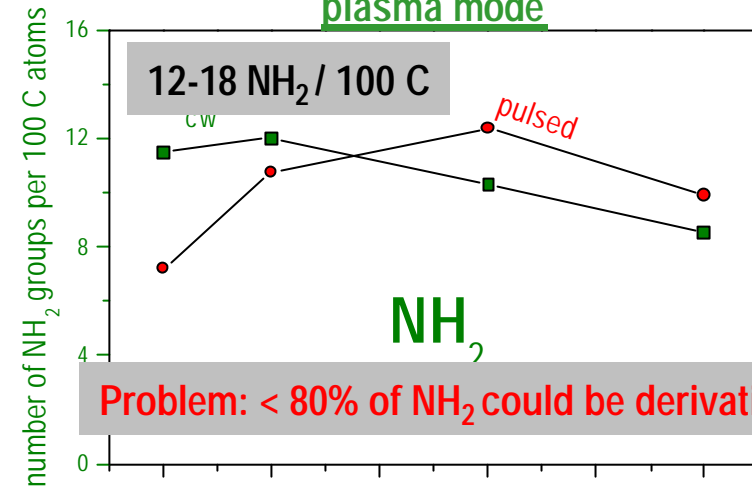
poly(allyl alcohol) OH - no OH deficit during storage

poly(acrylic acid) COOH - no COOH deficit during storage

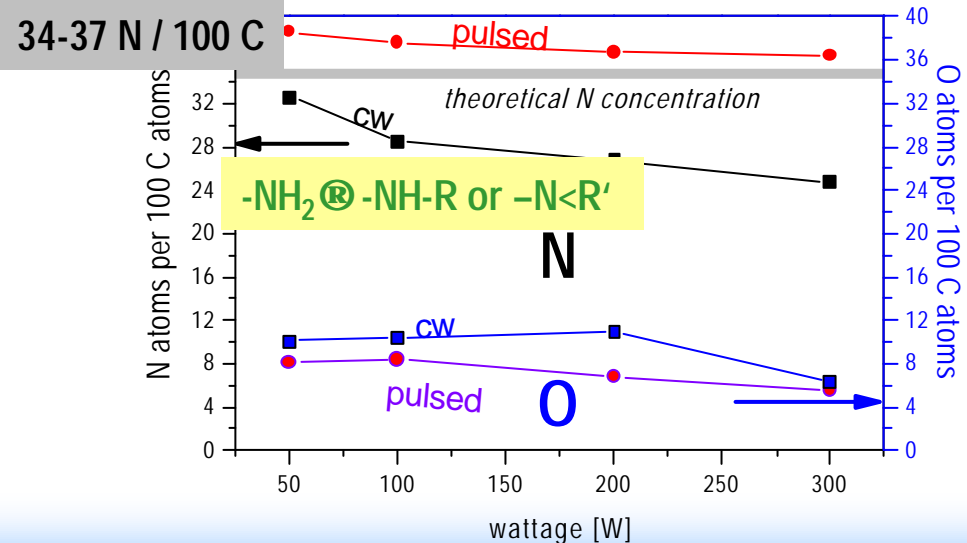
poly(allylamine) NH₂
 - reaction at NH₂ group
 - post-plasma introduction of > 15% O



NH₂ retention in allyl amine plasma polymer in dependence on wattage and plasma mode



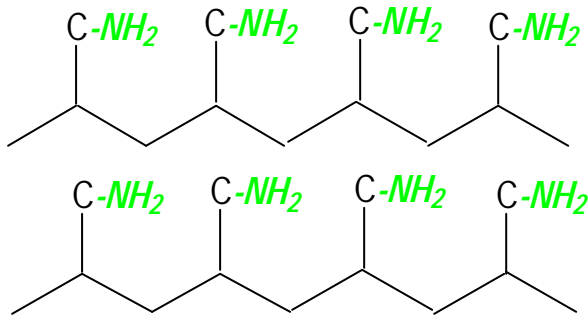
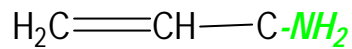
Problem: < 80% of NH₂ could be derivatized



Functional groups carrying plasma copolymers

Copolymerization

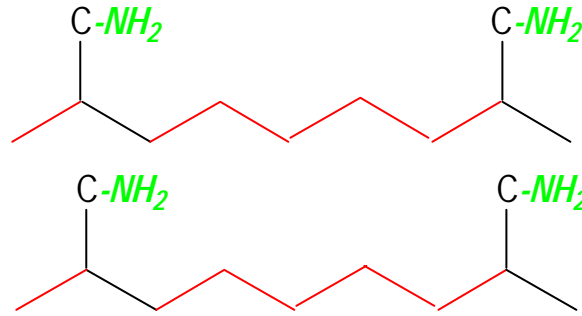
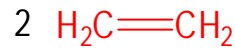
functional group carrying comonomers and **chain-extending** comonomers
for **varying the density** of functional groups or
functional group carrying comonomers and **bifunctional** comonomers
for **chemical crosslinking**



homopolymerization



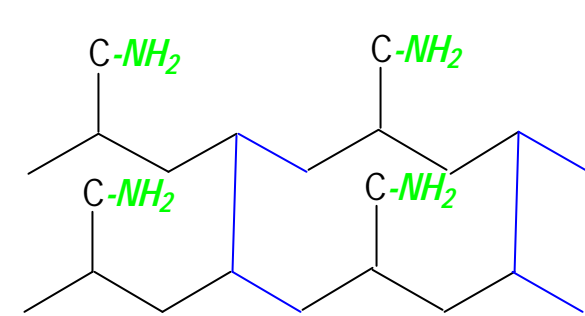
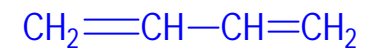
+



copolymerization



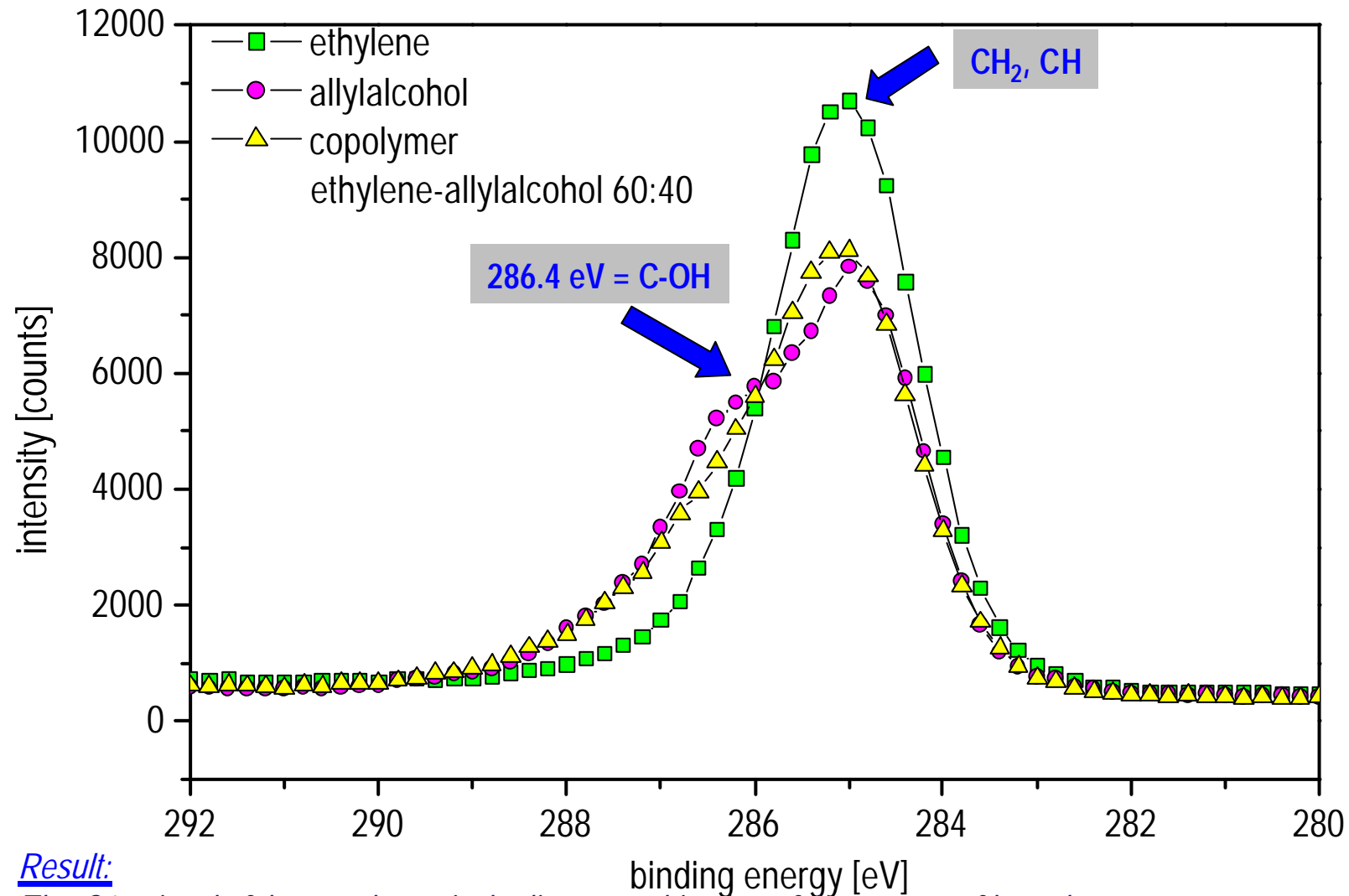
+



chemical crosslinking

Copolymerisation

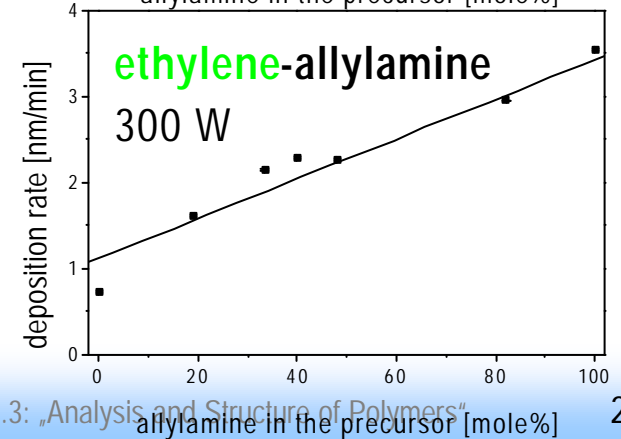
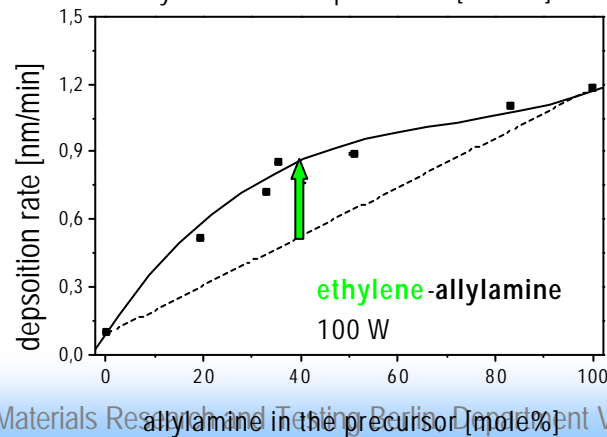
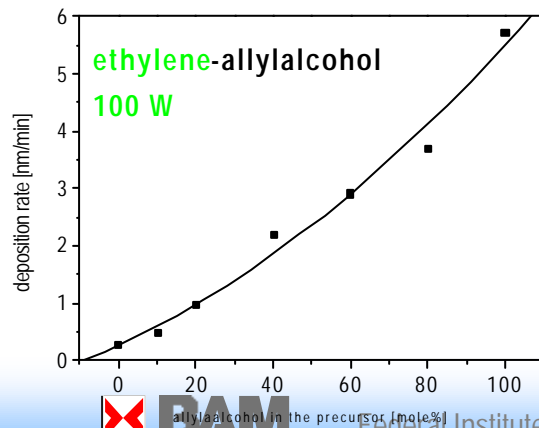
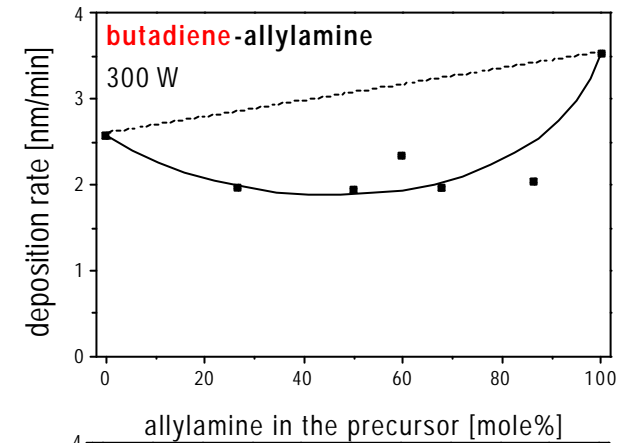
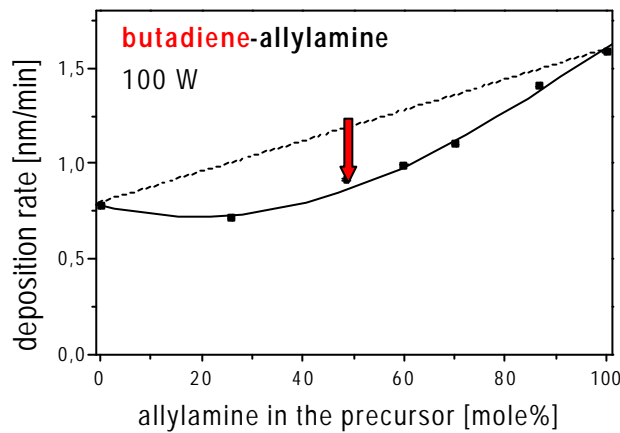
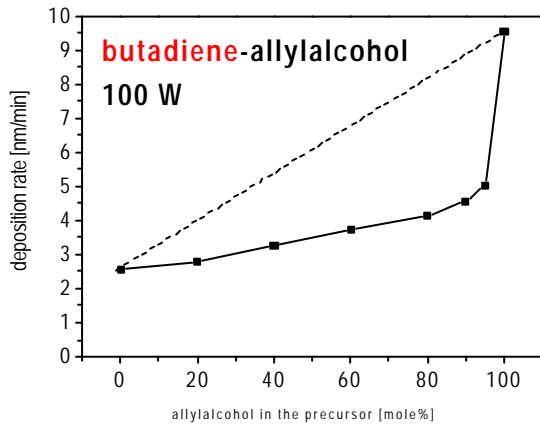
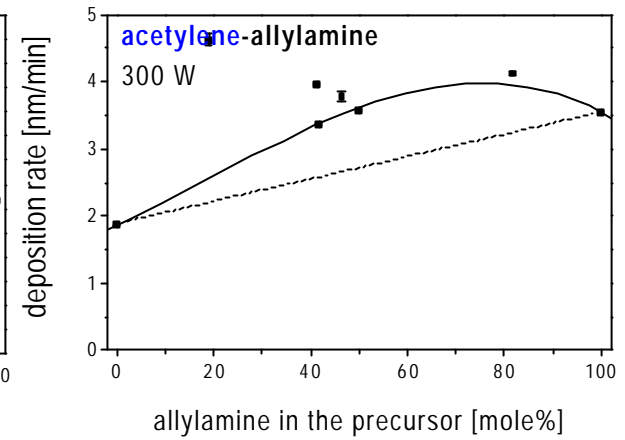
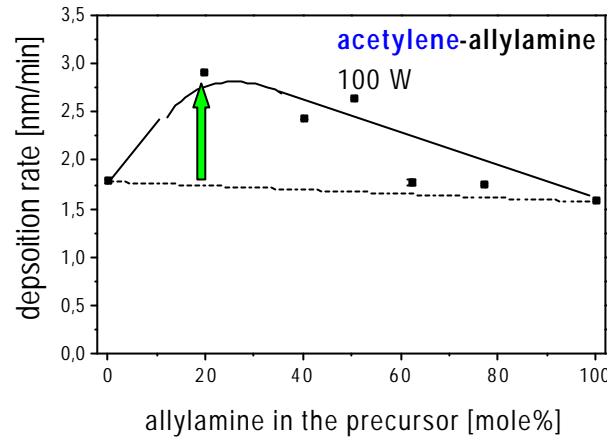
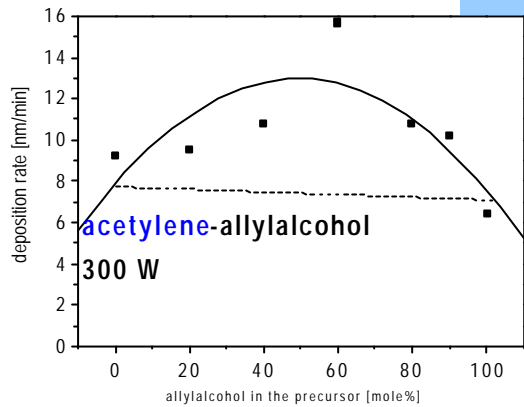
C1s peaks of pulsed plasmapolymers of ethylene, allyl alcohol and ethylene-allyl alcohol copolymer



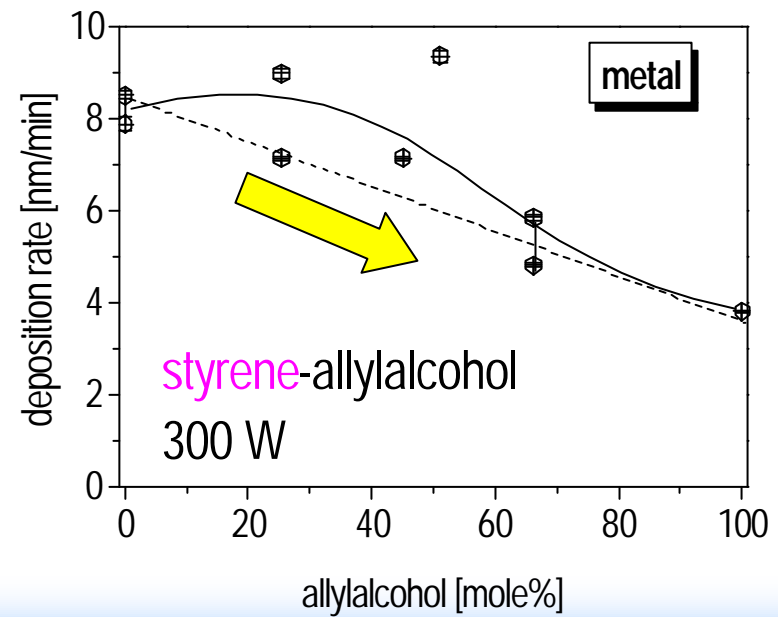
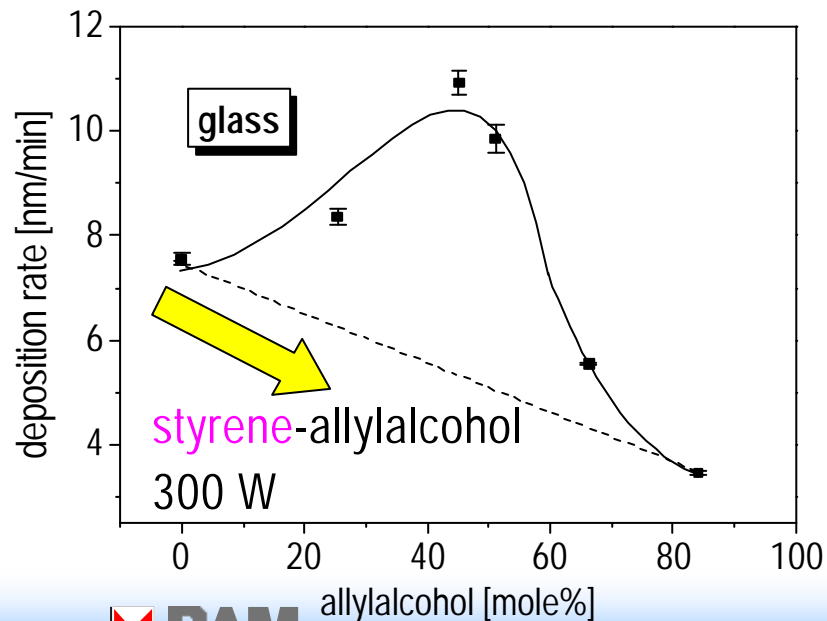
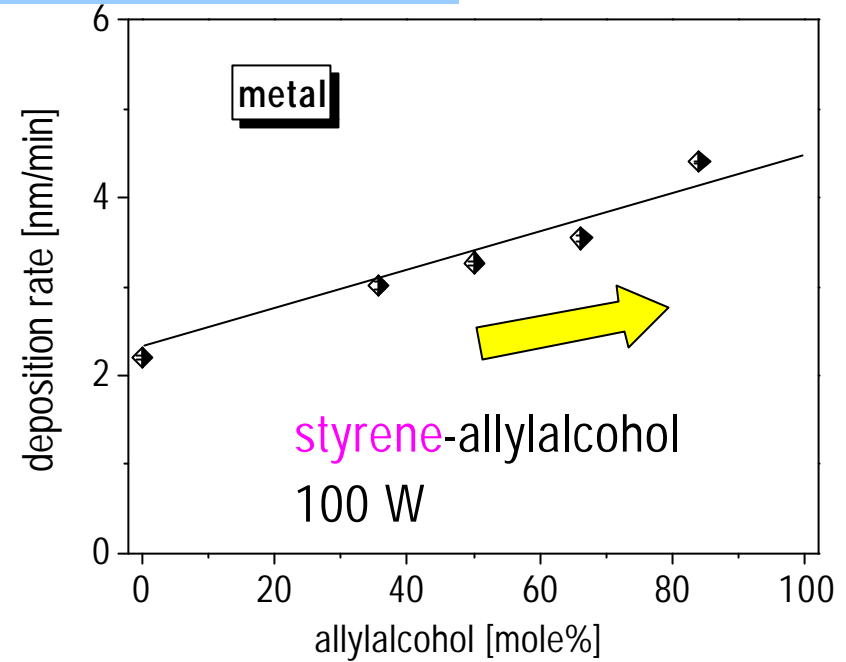
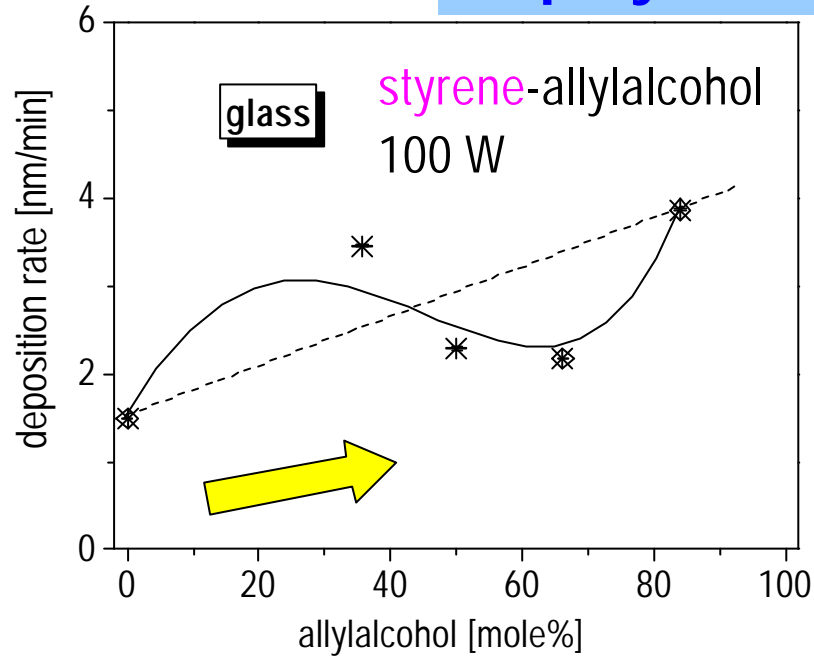
Result:

The C1s signal of the copolymer is the linear combination of the spectra of homopolymers

Copolymerisation – deposition rates

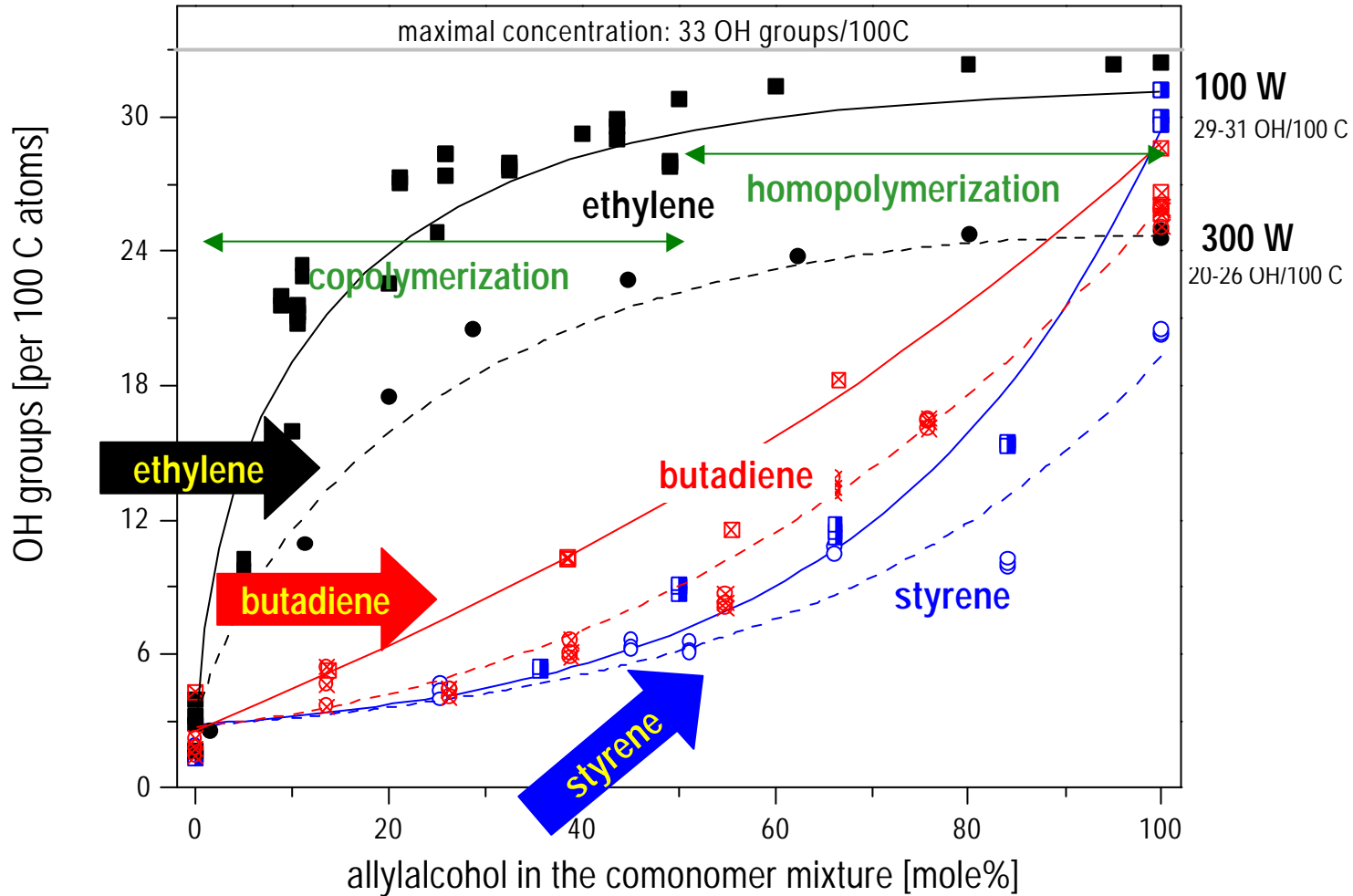


Copolymerisation – deposition rates



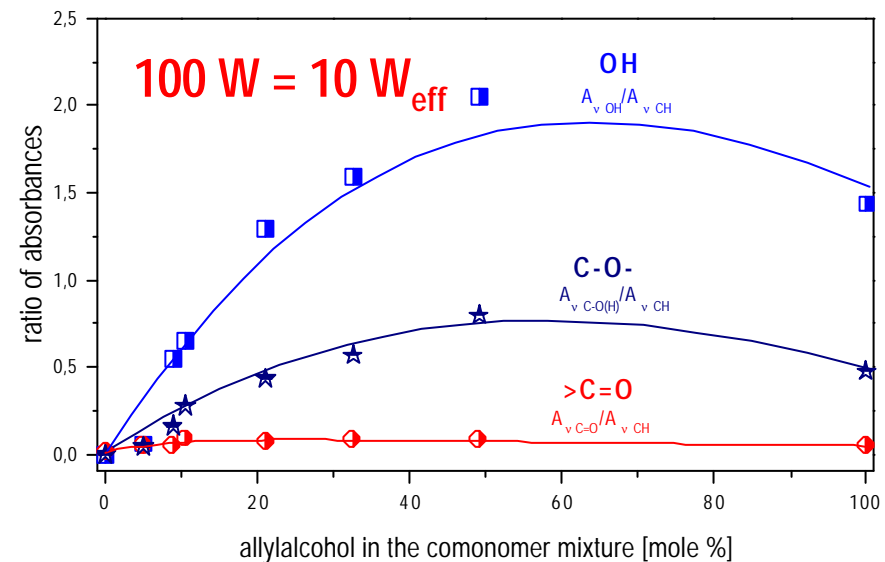
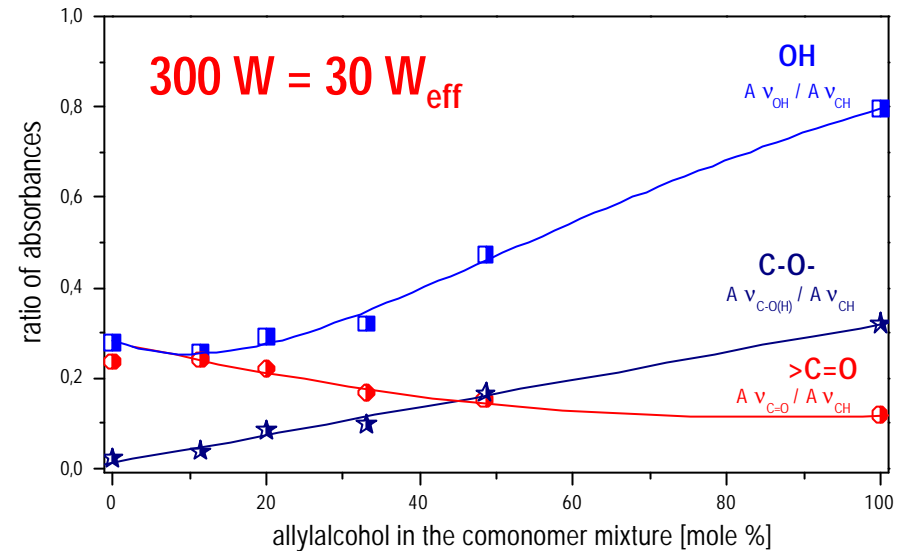
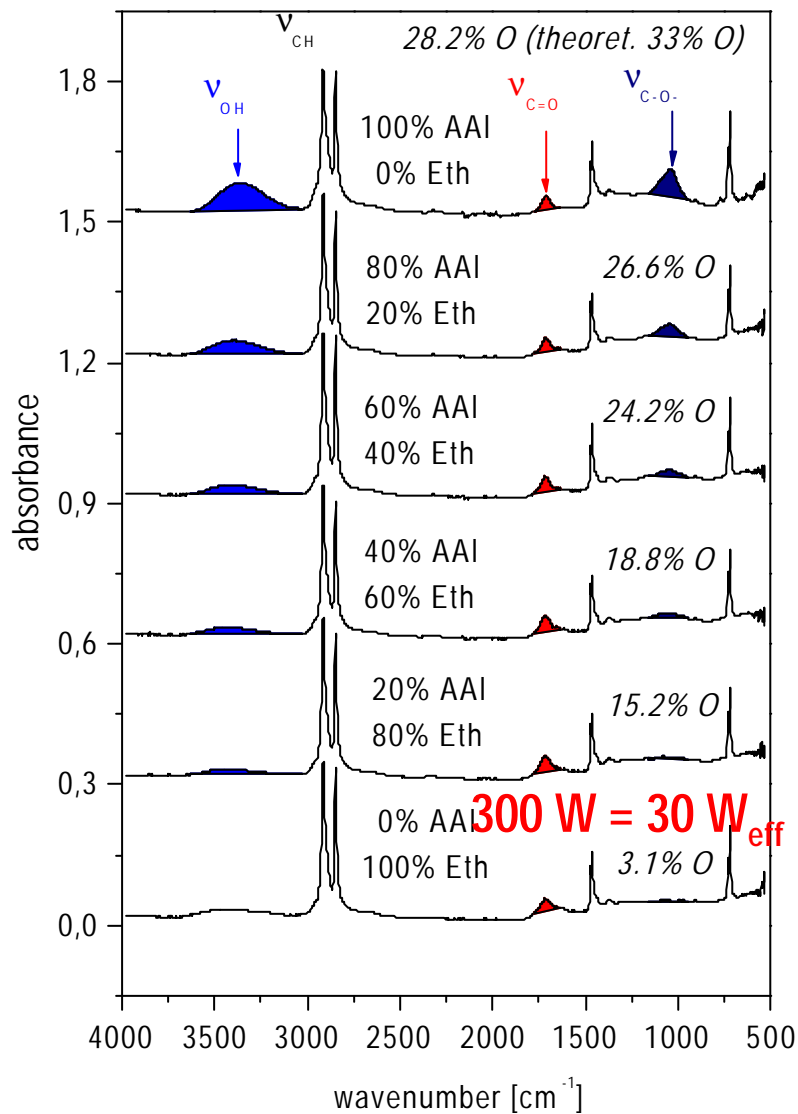
Copolymerization

XPS measured densities of OH groups of an ethylene-allyl alcohol, a butadiene-allyl alcohol and a styrene-allyl alcohol copolymer using the derivatization with TFAA



Copolymerization

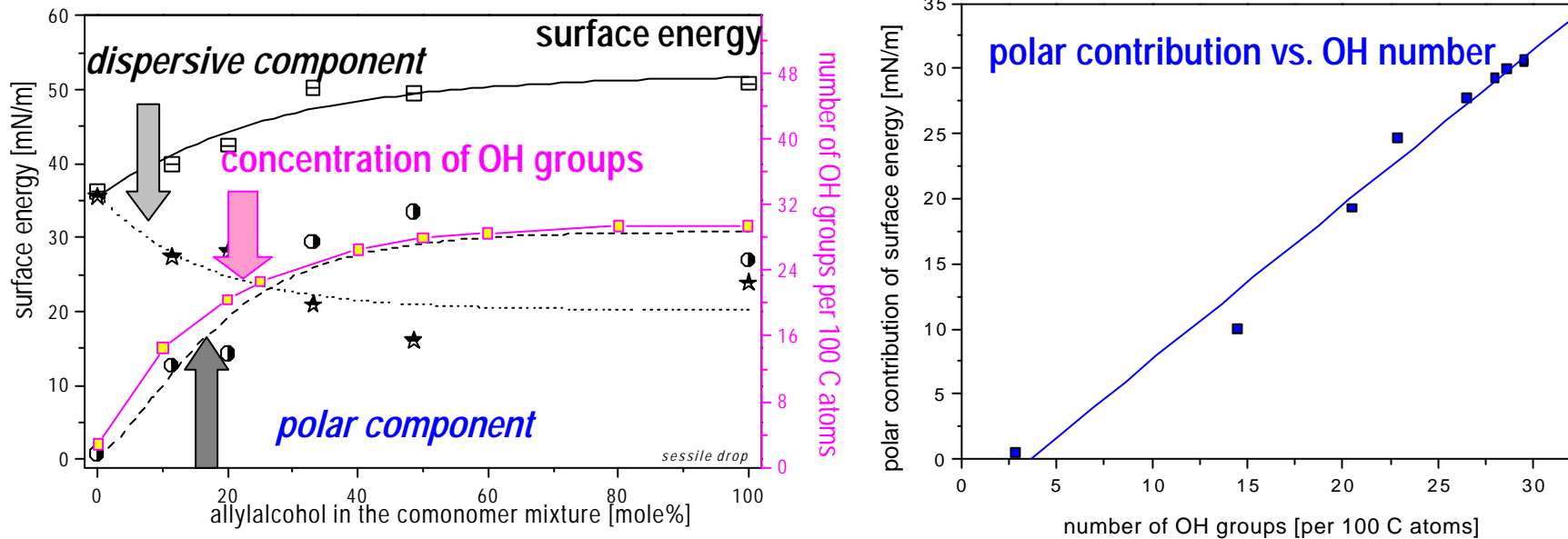
FTIR measured measured ν_{OH} of an ethylene-allyl alcohol copolymer



Copolymerization

surface tension of an ethylene-allyl alcohol copolymer

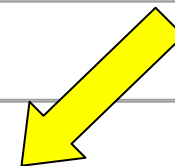
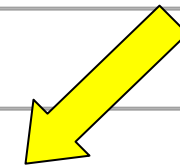
300 W



Result: The number of OH groups correlates with the polar contribution to the surface energy

Results of maximum polymer surface functionalization by applying different plasmachemical methods

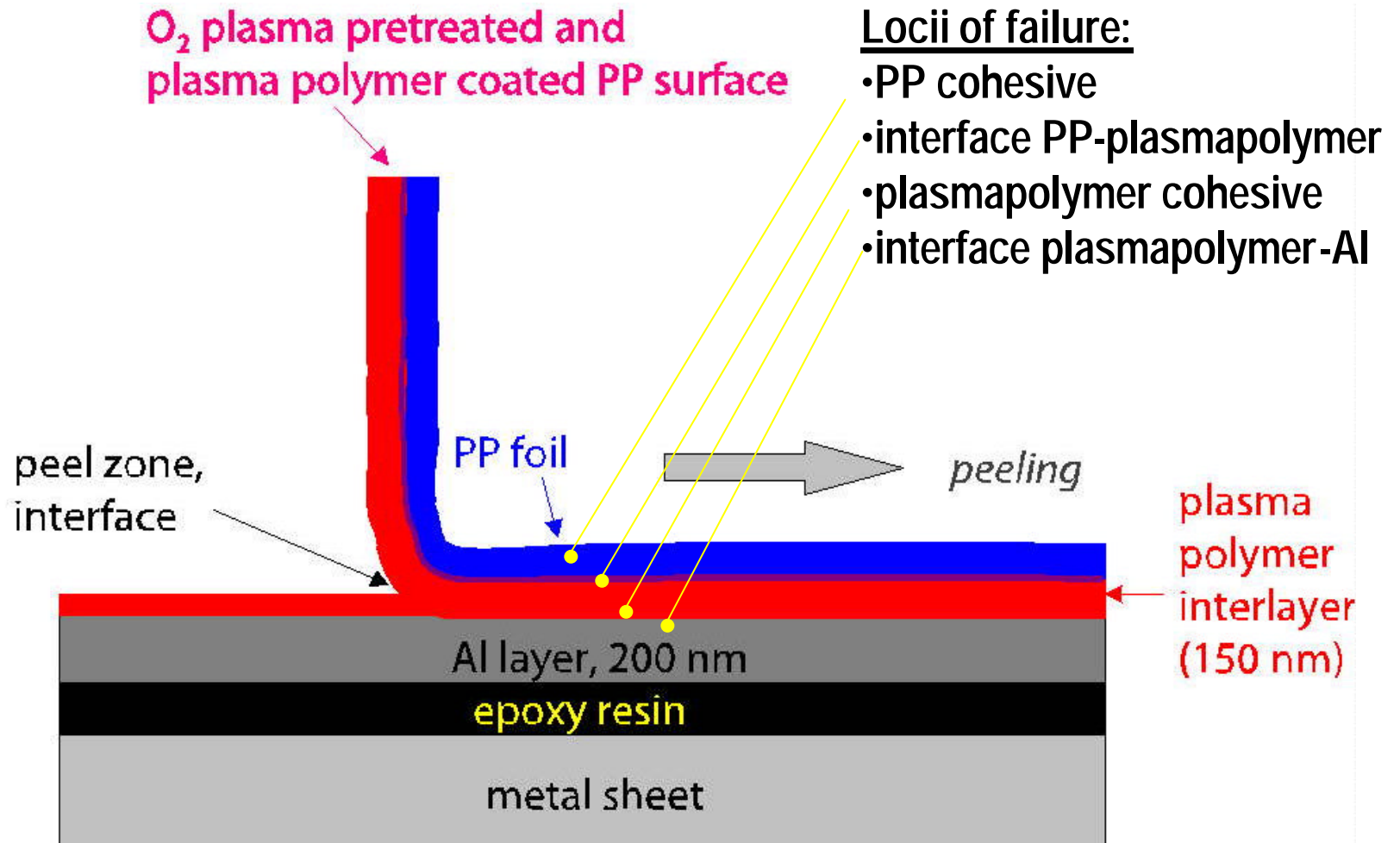
	<i>Process</i>	<i>Yield [%]</i>	<i>Selectivity [%]</i>
1	O ₂ plasma and B ₂ H ₆ reduction	10...14	55
2	Grafting to radicals	2...7	≈35
3	Bromination	20...40	85
4	Grafting of spacers	4...9	80
5	Homopolymerization-OH	28...31	85-95
5	Homopolymerization-NH ₂	12...18	40-55
5	Homopolymerization-COOH	18...24	55-75
6	Copolymerization	0-31	55-95



Metal-polymer interactions

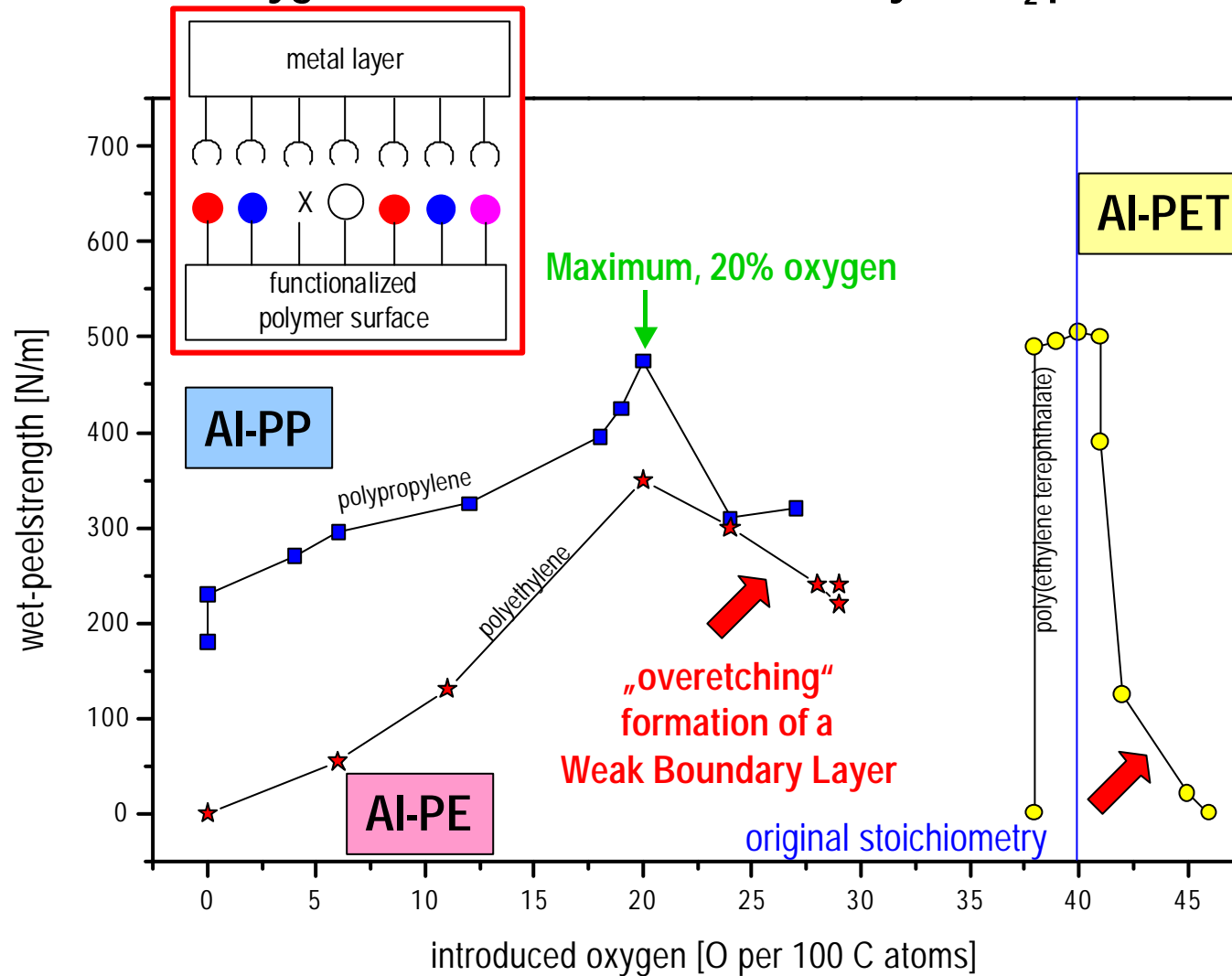
Metal-polymer adhesion

Peel specimen of PP-Al composites with pulsed plasma polyallyl alcohol, allyl alcohol-ethylene, allylamine, allylamine-ethylene and acrylic acid polymer and copolymer interlayers as adhesion promoters



Metal-polymer adhesion

Dependence of peel strength of thermally evaporated Al on the concentration of oxygen at the surface introduced by the O₂ plasma treatment

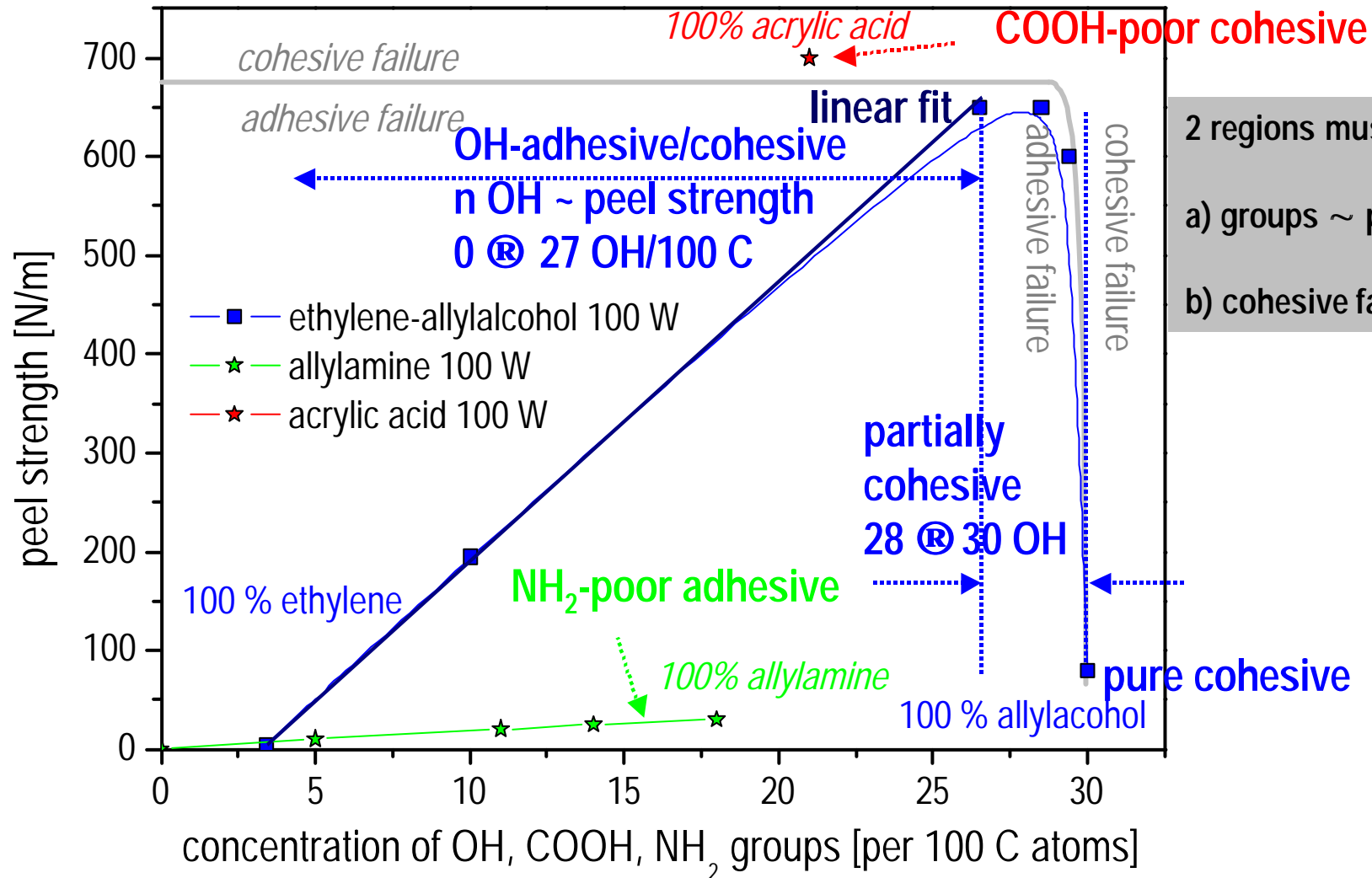


With increasing plasma-enhanced introduction of oxygen, using the O₂ plasma, the peel-strength of thermally evaporated Al onto PP and PE was maximum at **20 O atoms** per 100 C atoms. Higher values of oxygen were connected with the degradation of the polymer and the formation of a weak boundary layer.

With PET small variations of the **original** percentage of oxygen (**stoichiometry**) were also related with the degradation of the polymer and the formation of a weak boundary layer.

Metal-polymer adhesion

Dependence of AI peel strengths on type and density of functional groups at polymer surfaces



2 regions must be decided:
a) groups ~ peel strength
b) cohesive failure

Summary

➤ 6 processes for monotype polymer functionalization were compared:

- O₂ plasma + chem. reduction = 11 OH/100C
- grafting onto C radicals = 5 NH₂/100C
- bromination = 40 Br/100C
- spacer-OH onto OH or Br = 8 sp/100C
- pulsed plasma polymerization = 31 OH/100C
- copolymerization = 0...31 OH/100C

- the introduction of O functional groups onto polymer surfaces by oxygen plasma is finished after **2 s**
- in maximum **60%** of all O functional groups can be reduced chemically to OH
- prolonged exposure of different types of polymers to oxygen plasma results in:
 - random degradation
 - crosslinking
 - photo-oxidative degradation
 - depolymerization
- Crosslinking is finished after 10 s
- plasma **bromination is a highly selective** and direct way of polymer surface functionalization

- The formation of pulsed plasma polymers of vinyl, acrylic and also allyl monomers is dominated by the **plasma-initiated** (plasma-on) **gas-phase radical polymerisation** (plasma-off)
- **Olefines** were used as “**chain-extenders**” in the copolymers, **dienes** as “**chemical crosslinkers**” and **functional groups carrying** comonomers in the **plasma-initiated copolymerisation**
- The composition of polymers/copolymers was close to those of reference polymers. However, a significant number of irregularities are also involved, most important **branched structures**
- Functional groups bearing monomers were pulsed plasma polymerised with a degree of retained functional groups of Following functional groups could be produced: **31 OH, 18 NH₂, 24 COOH** per 100 C atoms (**55-95%** selectivity)
- The peel strength of Al on plasma polymers containing **COOH groups was the highest**, followed by OH groups and NH₂ groups without any adhesion promoting effect
- Varying the density of OH groups (by copolymerisation) **the peel strength was maximum at high densities of OH groups** or using **COOH groups**.