Polymer Structure

elucidated by

Mass Spectrometry

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ASMS Fall Workshop 2004 Polymer Structure Baltimore Dec. 9-10

Max Planck Institute for Polymer Research

Outline

- Structure determination of monodisperse macromolecules
  - Phenylene dendrimers
  - Giant polycyclic aromatic hydrocarbons (PAH's)
- Structure determination of polydisperse macromolecules
  End group determination of homo-polymers
  - in simple cases (Poly(styrene))
  - in difficult cases (Poly(carbonate) and Poly(fluorene))
- Copolymers
  - PPE-b-PEO Diblock-copolymer
  - Random copolymers of amino acids

Analysis of a well defined phenylene dendrimer by MALDI-TOF MS

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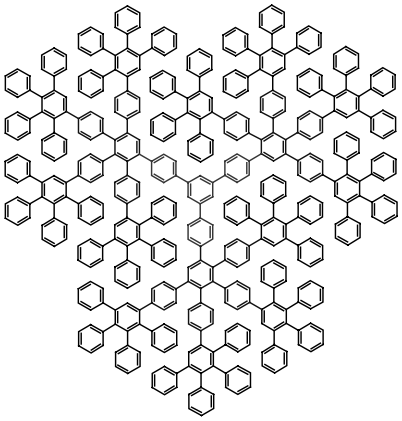

$C_{474}H_{318}$

MALDI-TOF Analysis of a soluble C474 Dendrimer

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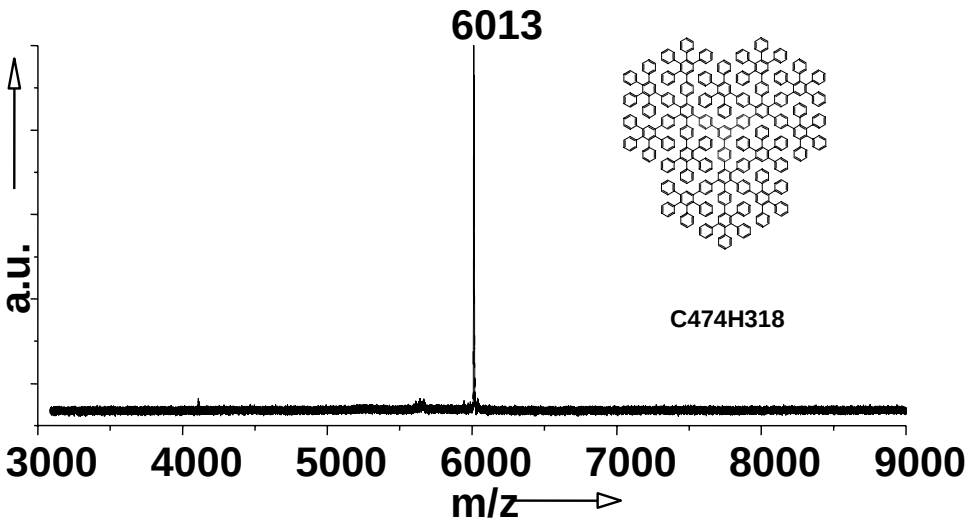

C474H318

Measured and Simulated Isotopes of $C_{474}H_{318}$ -Dendrimer

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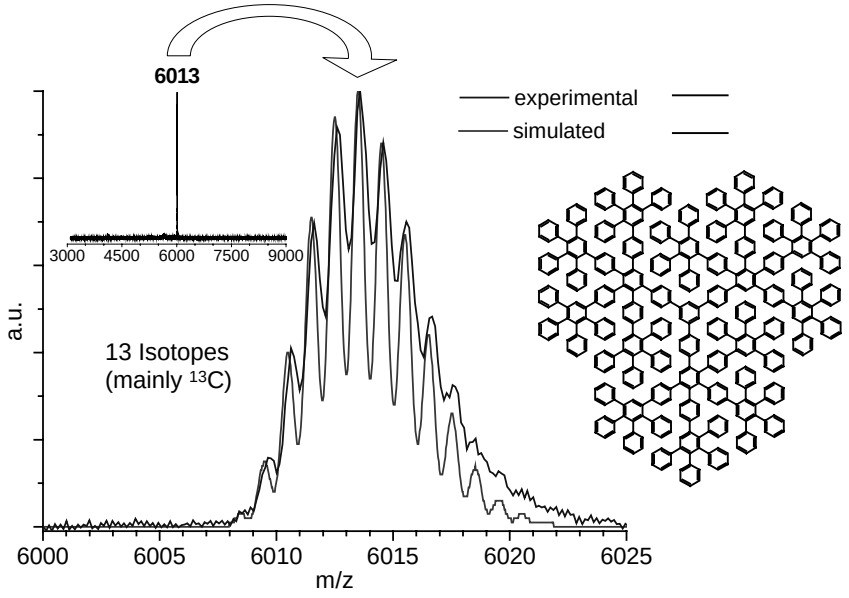

Synthesis of a C222 - PAH - disc

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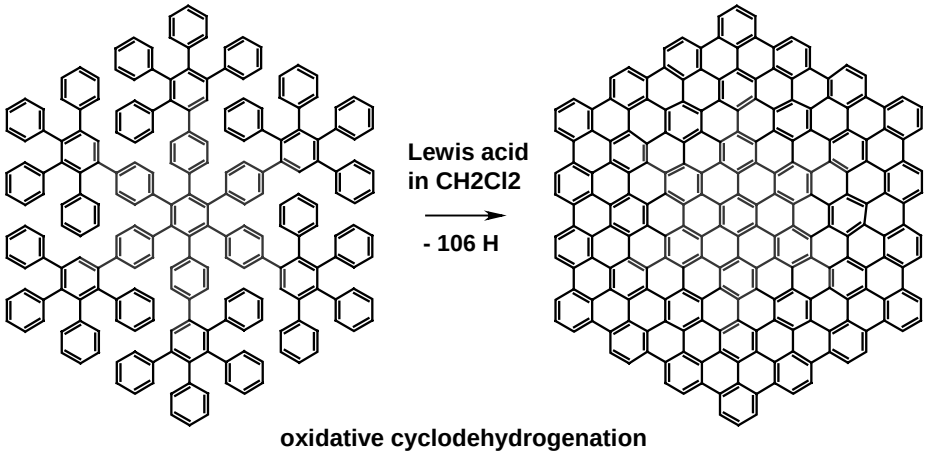
Reaction Scheme

soluble dendritic precursor

insoluble PAH product



oxidative cyclodehydrogenation

MALDI-TOF-Mass Spectrum with TCNQ as Matrix

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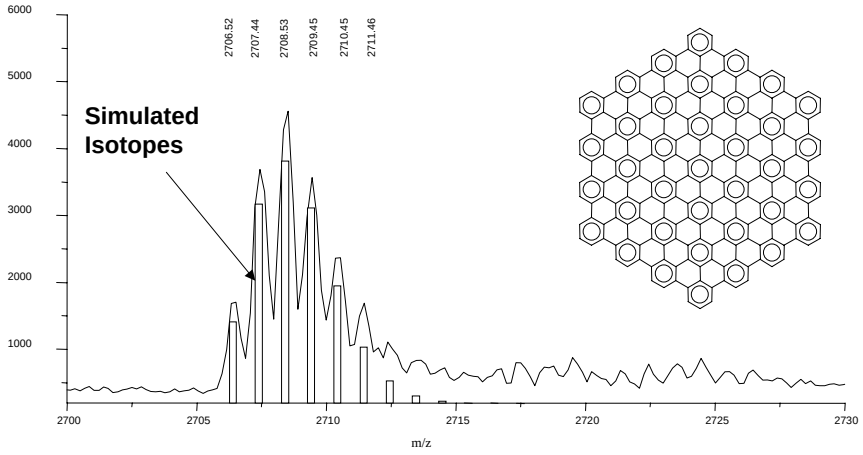
$C_{222}H_{42}$

2706.33

Characterization Method for Insoluble Samples



MALDI sample preparation

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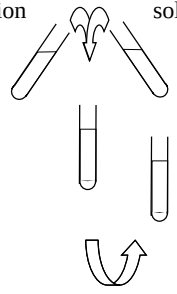
Commonly mixing dissolved samples and matrix in molar ratios of 1 : 1000

crucial step 1:

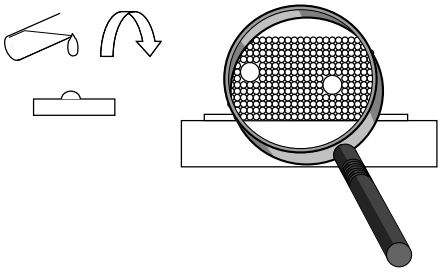
matrix solution

analyte solution



homogenous solution

crucial step 2:
(risk of phase separation)



homogenous crystal formation

Solvent-free sample preparation

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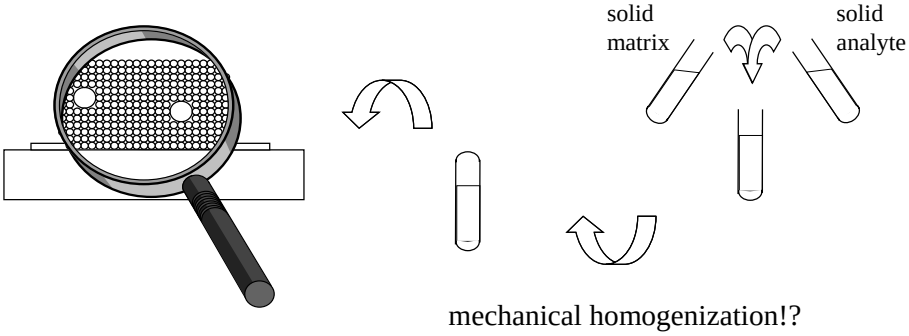
Mechanical mixing of solid samples in e.g. a ball mill

crucial step 2 is overcome!
No risk of phase separation

crucial step 1:



mechanical homogenization!?

Structure Defects

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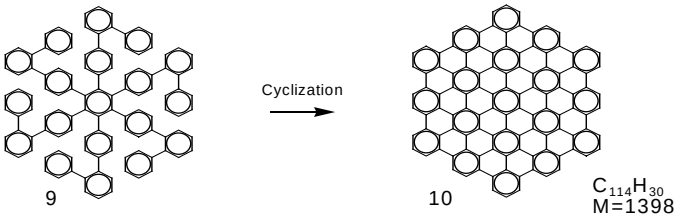
Product mixture with different numbers of hydrogens



a

Incomplete Cyclodehydrogenation?

Structure Defects

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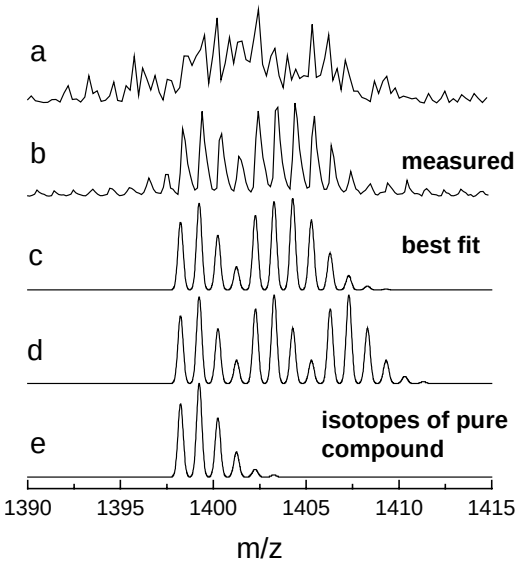
crude powder (product)

product dispersion in TCE

simulation of mixture with
C114H30 : C114H34 : C114H36
1 : 1 : 0.54

simulation of mixture with
C114H30 : C114H34 : C114H38
1 : 1 : 1

simulation of C114H30



Possible side reactions (but unlikely)

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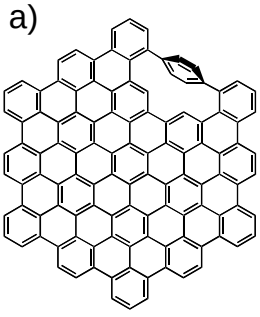
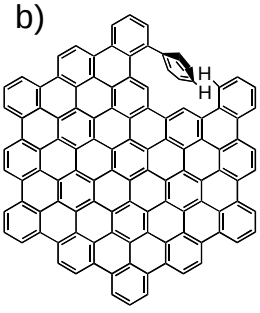
a)



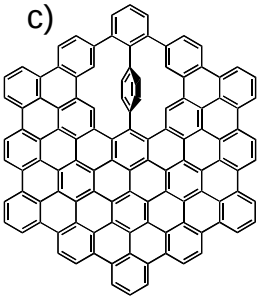
$C_{114}H_{34}$(m=1402m/z)

b)



$C_{114}H_{36}$(m=1404m/z)

c)



$C_{114}H_{38}$(m=1406m/z)

Incomplete cyclodehydrogenation reaction

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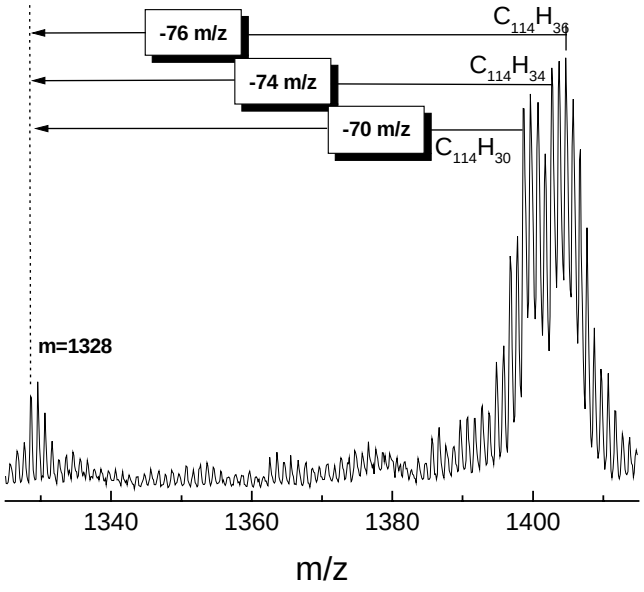
Fragmentation by In-Source-Decay (ISD)

No selection of precursor Ion possible



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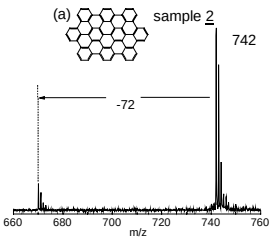
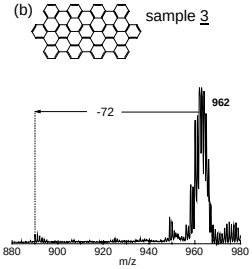
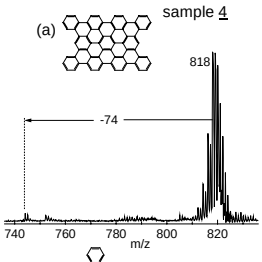
Structure Dependent Differences in Fragmentation Pattern

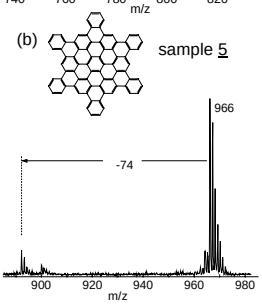
(1) arrow type



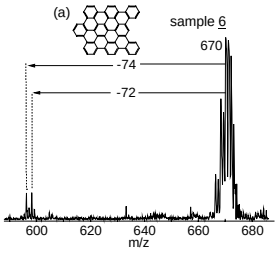


(2) bay type





(3) arrow & bay type



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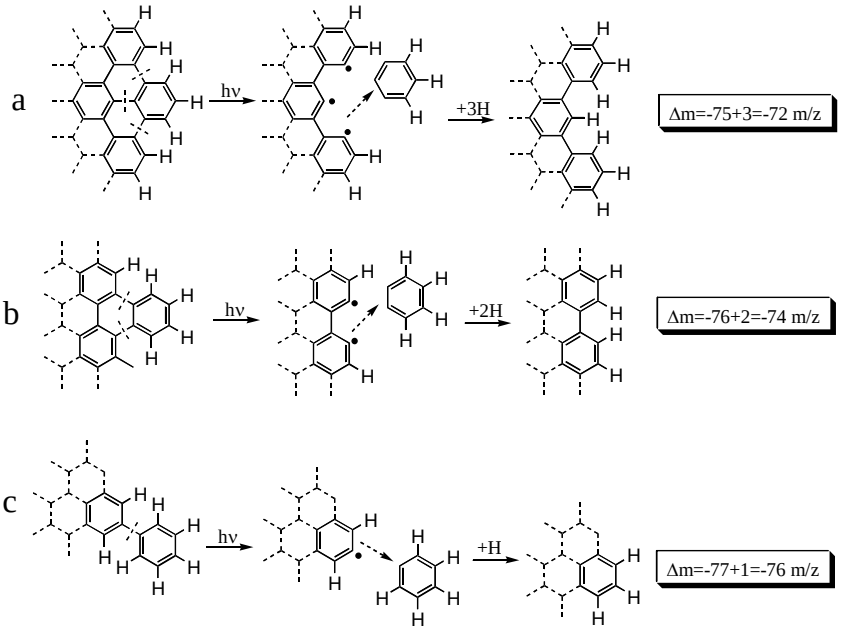
Loss of Cyclic C6 Units and Subsequent Rehydrogenation



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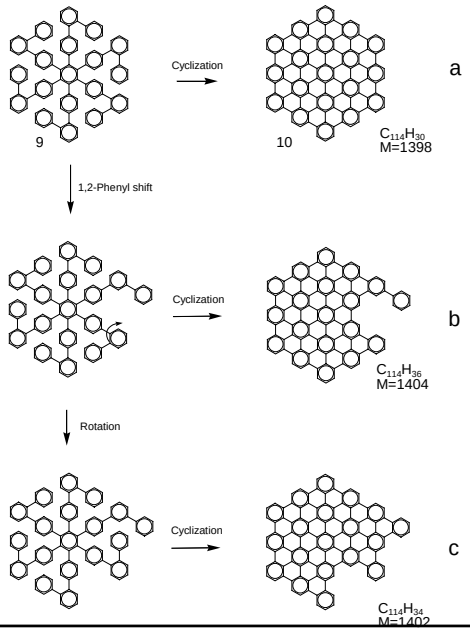
Plausible Side Products by Rearrangement Reactions



Cyclodehydrogenation Products of C474 Precursor

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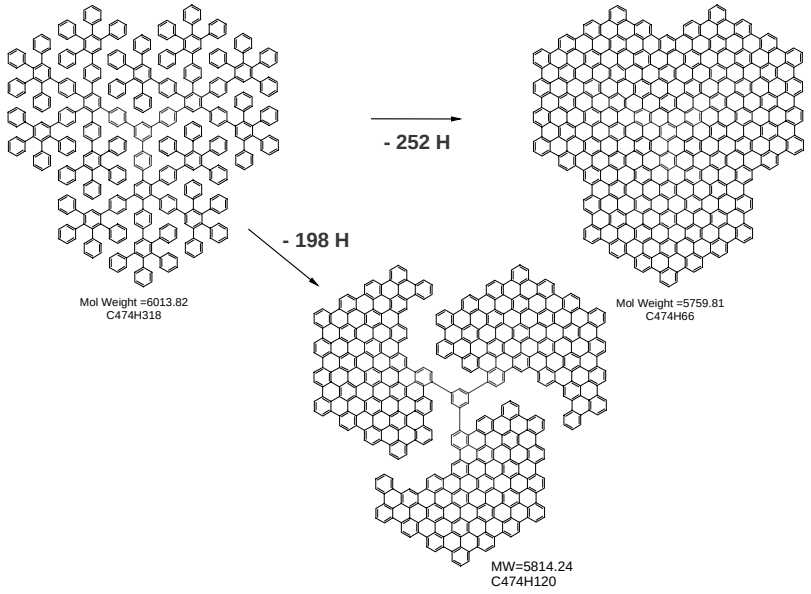

Spectra of different synthetic cyclodehydrogenation attempts

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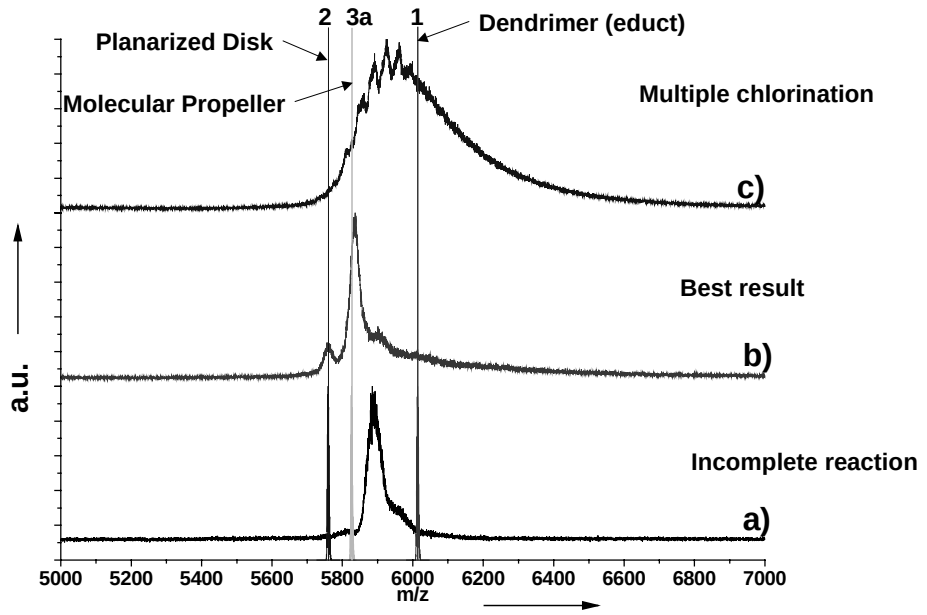

Computer generated visualization “C474 trimer“

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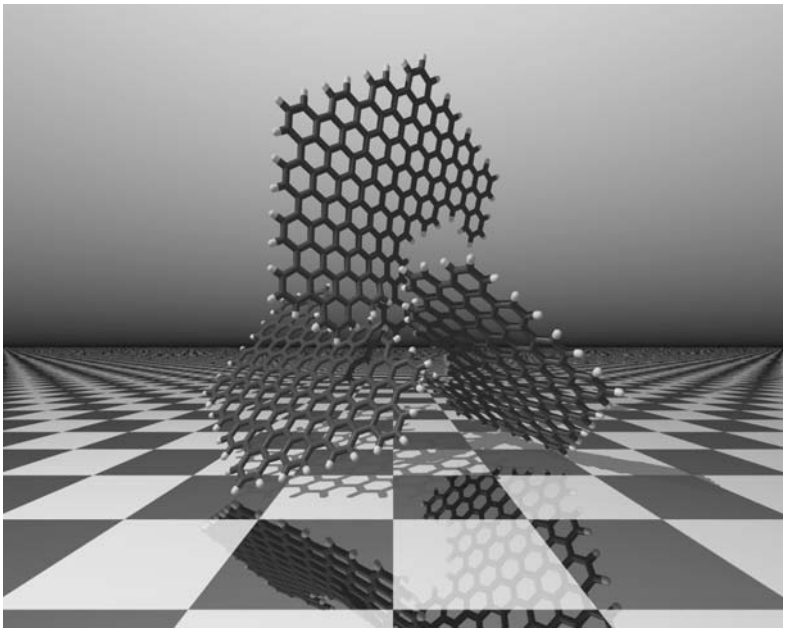

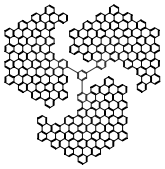

$C_{474}H_{120}$
M=5814

Molecular propeller

Solid-state UV-*vis* Spectrum of “C474 trimer“

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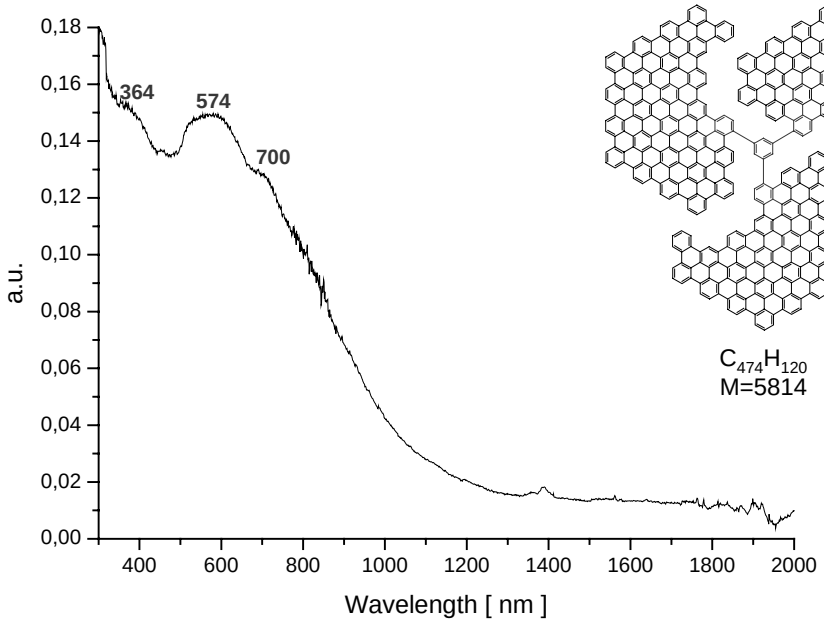
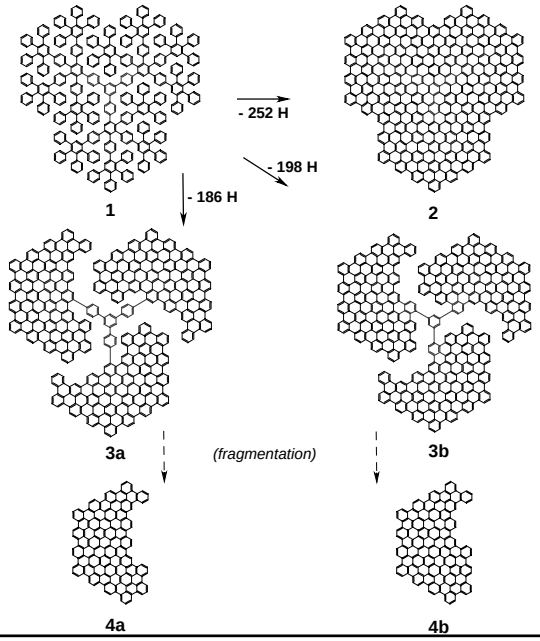
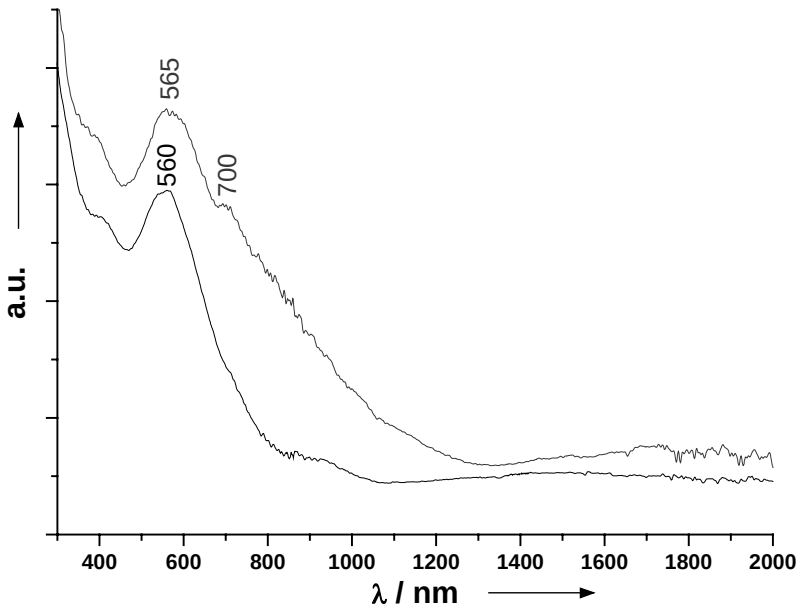


$C_{474}H_{120}$
M=5814


- 252 H
- 198 H
- 186 H
1
2
3a
3b
(fragmentation)
4a
4b


565
560
700
a.u.
400
600
800
1000
1200
1400
1600
1800
2000
λ / nm

Outline

- Structure determination of monodisperse macromolecules
  - Phenylene dendrimers
  - Giant polycyclic aromatic hydrocarbons (PAH's)
- Structure determination of polydisperse macromolecules
  End group determination of homo-polymers
  - in simple cases (Poly(styrene))
  - in difficult cases (Poly(carbonate) and Poly(fluorene))
- Copolymers
  - PPE-b-PEO Diblock-copolymer
  - Random copolymers of amino acids

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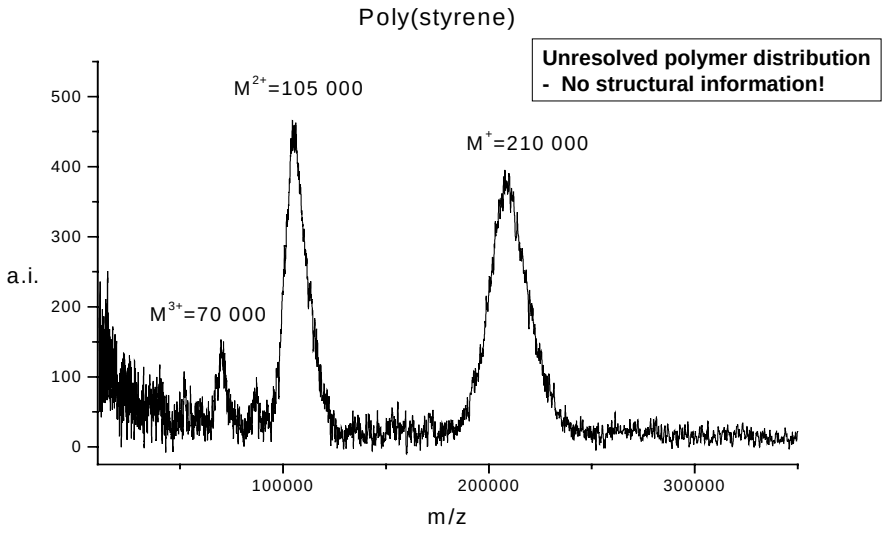
MALDI-TOF Spectrum of Poly(styrene) 210,000 Da



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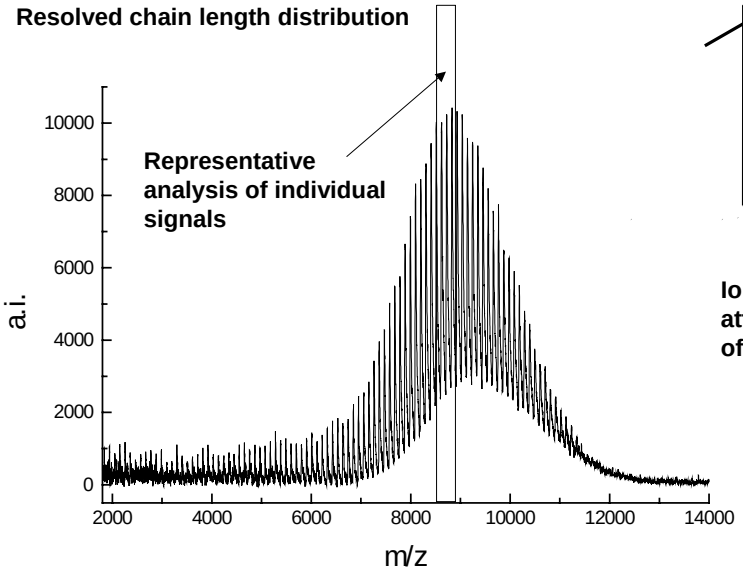
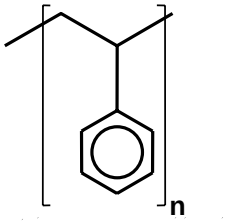
MALDI-TOF Spectrum of Poly(styrene) 9,000 Da





Ionized by attachment of Ag^+

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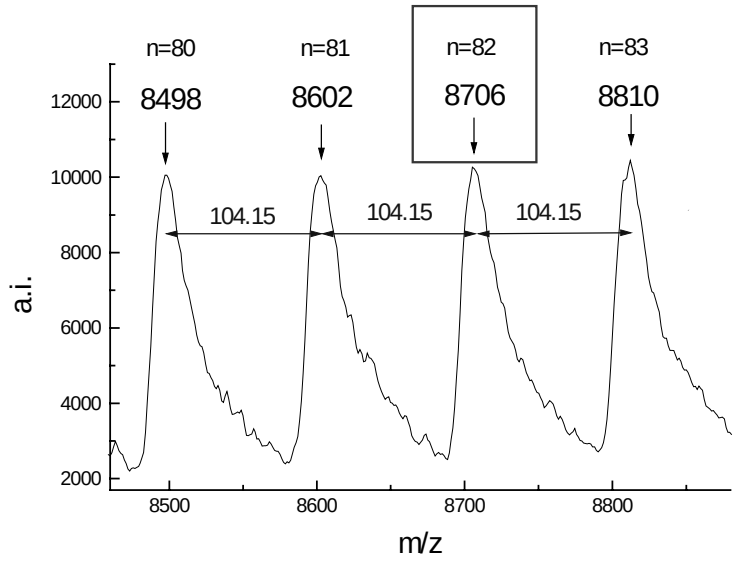
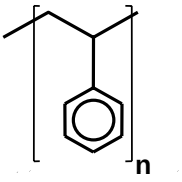
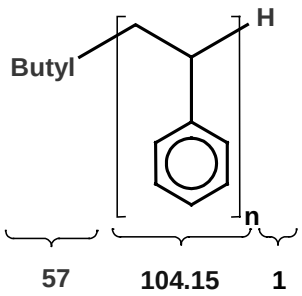
Mass of Repeat Units for Recognition of Polymer Type





C_8H_8 = 104.15
Styrene unit

Calculation of End Group Molecular Weight



Mass contributions:

8706 = 82 (n) * 104.15 (Styrene)
+ 57 (Butyl)
+ 1 (Hydrogen)
+ 108 (Ag^+)

End group calculation:

8706 - 108 (Ag^+) = 8598 (corrected polymer mass)
8598 : 104.15 (styrene unit) = 82.554 (repeat units)
82.554 ⟶ 82 styrene repeat units (n)
and decimal place bears end group mass:
0.554 * 104.15 = 57.7 (mass of both end groups)

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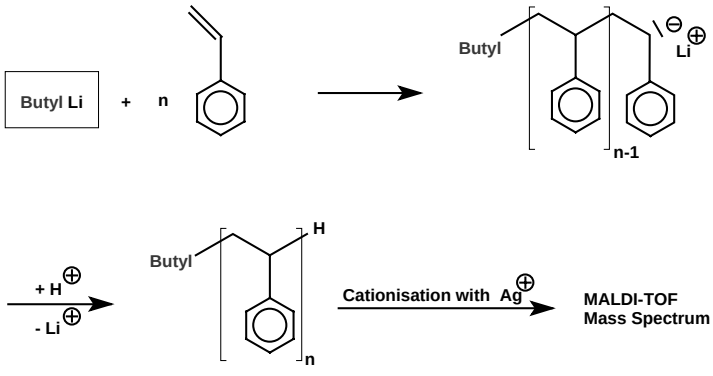
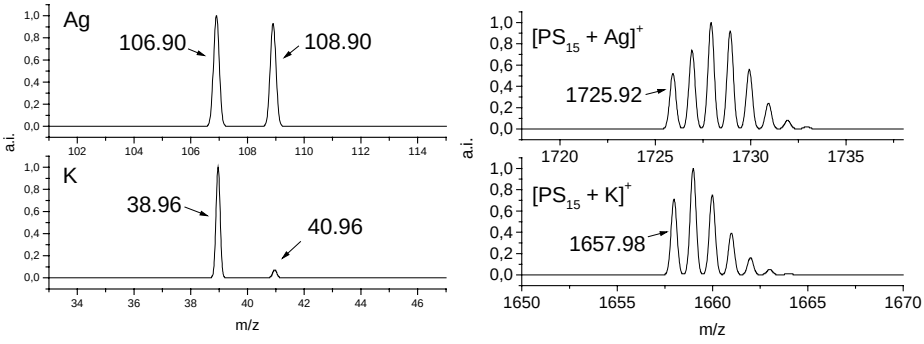
Sample History: Way of Synthesis

Anionic Polymerization of Styrene



Isotopic Pattern

Isotopic Distributions of a Polystyrene Chain of n = 15 (1619,02 Da) Ionized with Different Cations



Important for unambiguous interpretation: Knowledge of attached cation!

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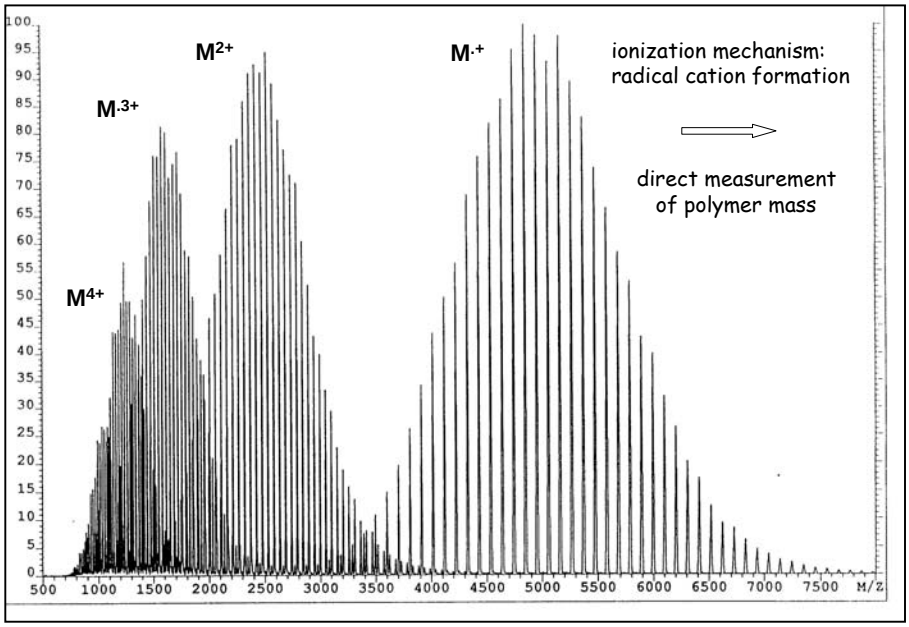
Field Desorption Spectrum of Polystyrene 5 kDa



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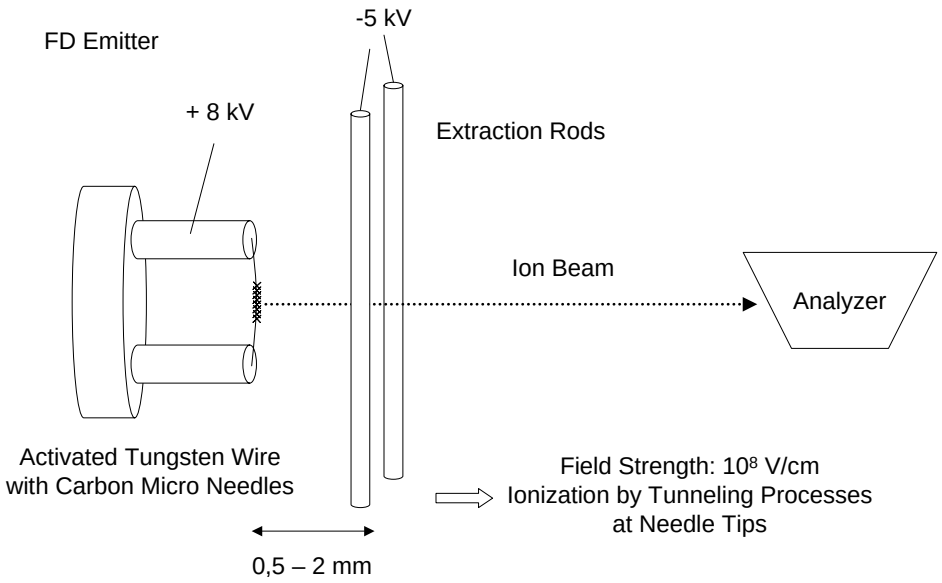
Principle of Field Desorption



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End group determination of homopolymers in difficult cases

End1 -[- repeat unit -]$_n$- End2

2 or even 3 unknowns → interpretation not straightforward

Expectations from fragmentation analysis: differentiation of chain ends

→ deduction of M_{End1}, M_{End2}, n

Investigated system: Polycarbonate - Elucidation of a spectrum with 7 superposed distributions

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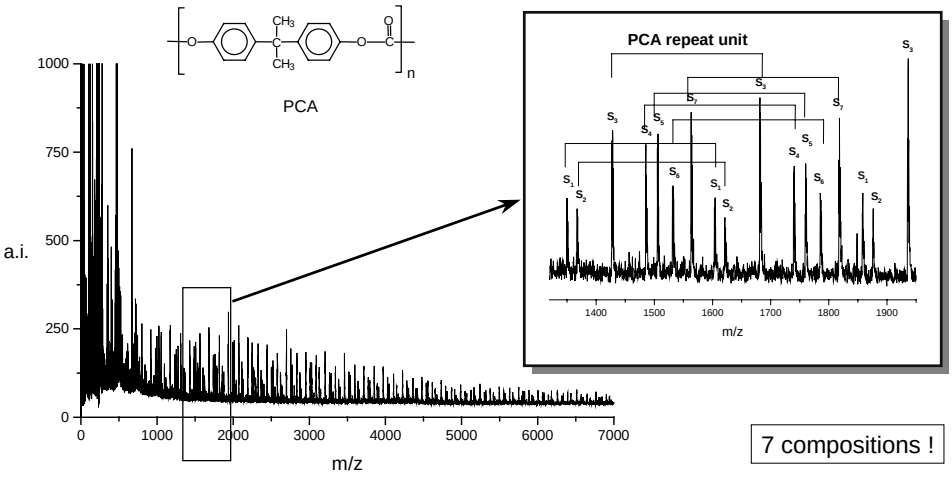
End group determination of a polycarbonate sample



7 compositions !

Conventional MALDI-TOF mass spectrum of a PCA sample

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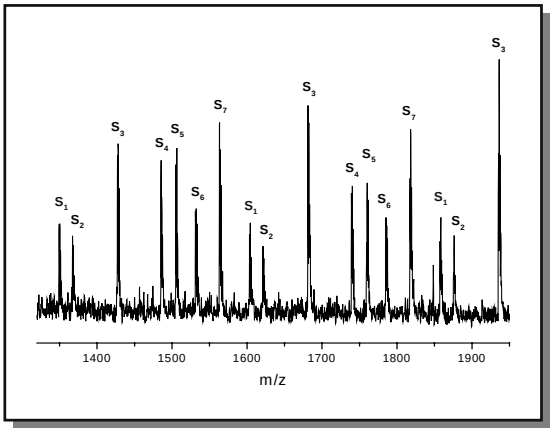
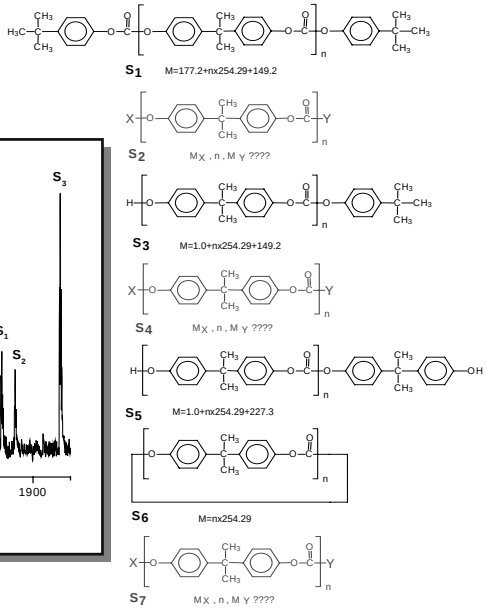
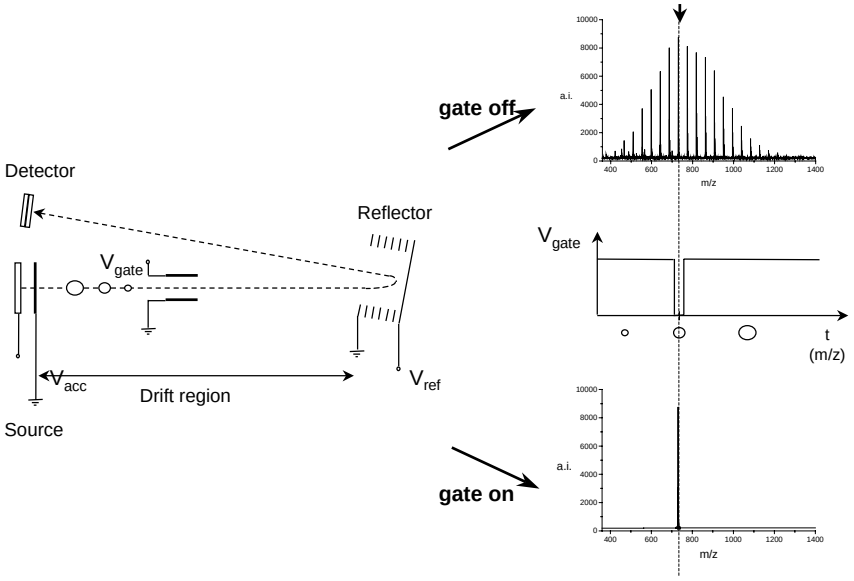
End group determination of a polycarbonate sample

Interpretation of conventional MALDI-TOF mass spectrum:

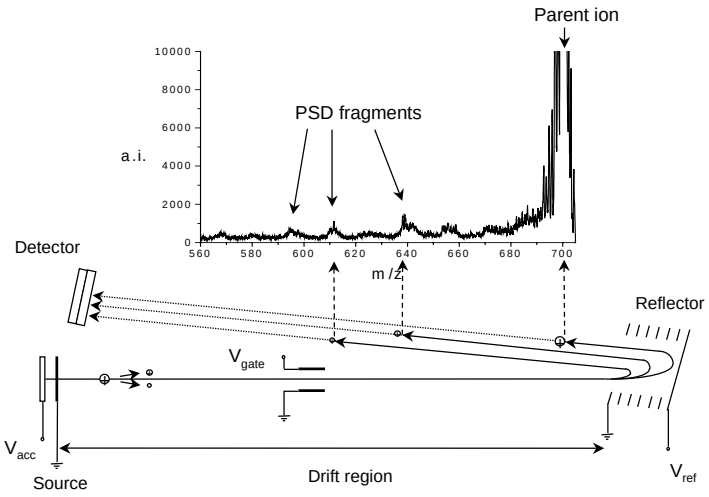




Selection of a defined signal for fragment ion analysis



Post-source decay



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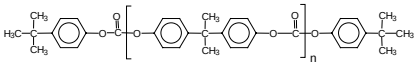
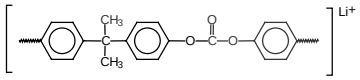
Polycarbonate: fragmentation mechanism?

Main fragmentation of PCA:

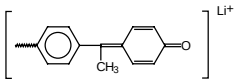


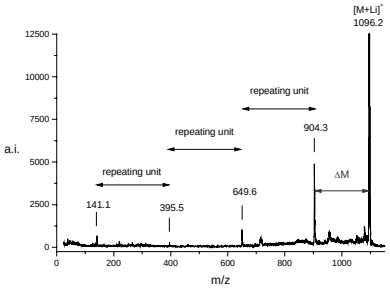


- CH3

and -

analogue to mechanism
described for EI, SSIMS (Literature)





Fragment mass spectrum

$\Delta M = M_{CH3} + M_{End}$
$= 15 + M_{End}$

→ M_{End} deduced !

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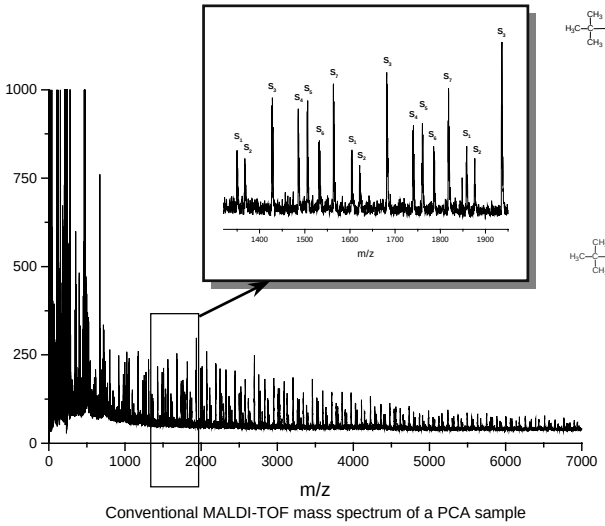
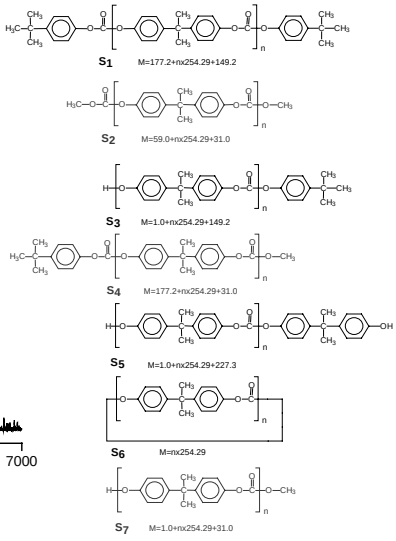
Result: Complete elucidation of the end group composition



Conventional MALDI-TOF mass spectrum of a PCA sample



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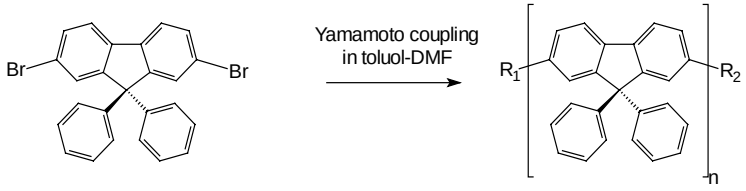
Synthesis of Polyfluorene (PF)



2,7-dibromo-9,9-diphenylfluorene

1

Poly(9,9-diphenyl-2,7-fluorene)
repeating unit: 316 Da

2

Dr. A. C. Grimsdale

2a: R1=Br; R2=Br
2b: R1=Br; R2=H or R1=H; R2=Br
2c: R1=H; R2=H
2d: R1=R2=no atom (cyclic structure)

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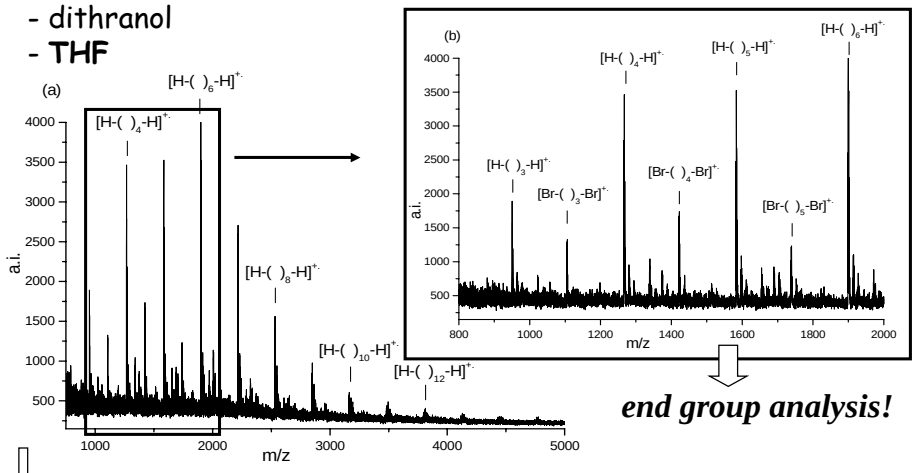
Solvent-Based MALDI MS of the Soluble Fraction (< 10%) of PF

- dithranol
- **THF**



end group analysis!

oligomerization degree ~ n = 15

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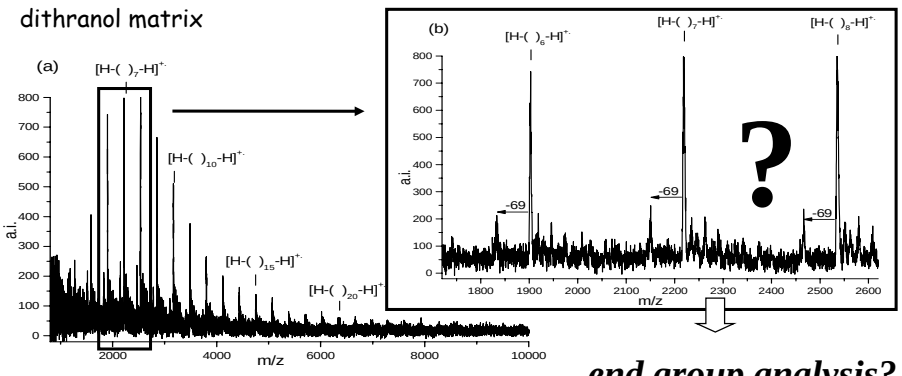
Solvent-Free MALDI MS of Insoluble Polymer Fraction (> 90%) of PF



end group analysis?

oligomerization degree ~ n = 25

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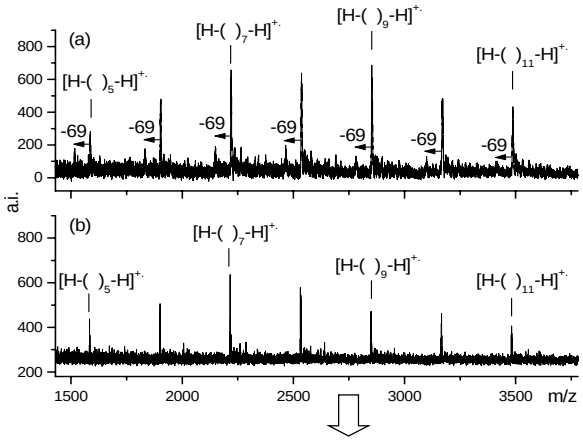
Influence of the MALDI Matrix



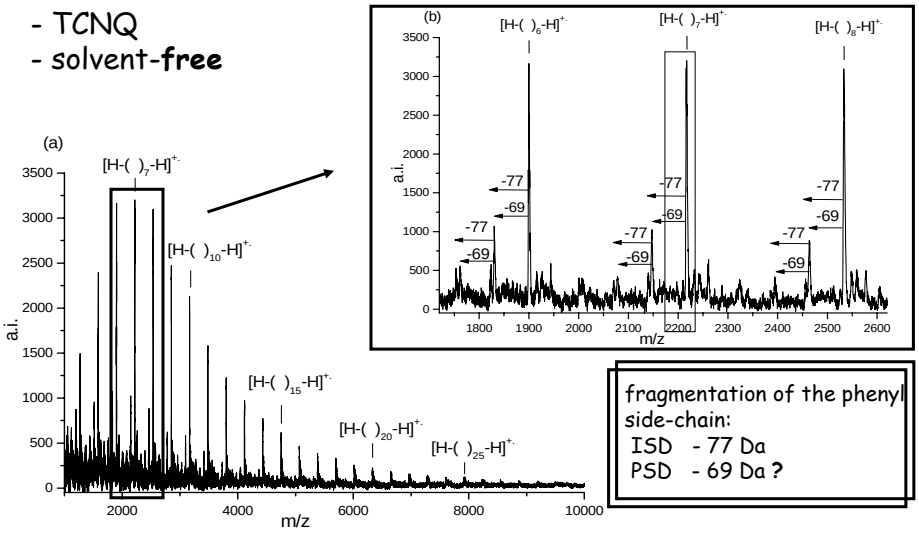
- **insoluble** fraction
- solvent-**free**
- **minimum** laser power
- **dithranol**

- **insoluble** fraction
- solvent-**free**
- **minimum** laser power
- **TCNQ**

successful suppression of fragmentation
& independence of matrix choice!

Insoluble Fraction of PF at High Laser Power

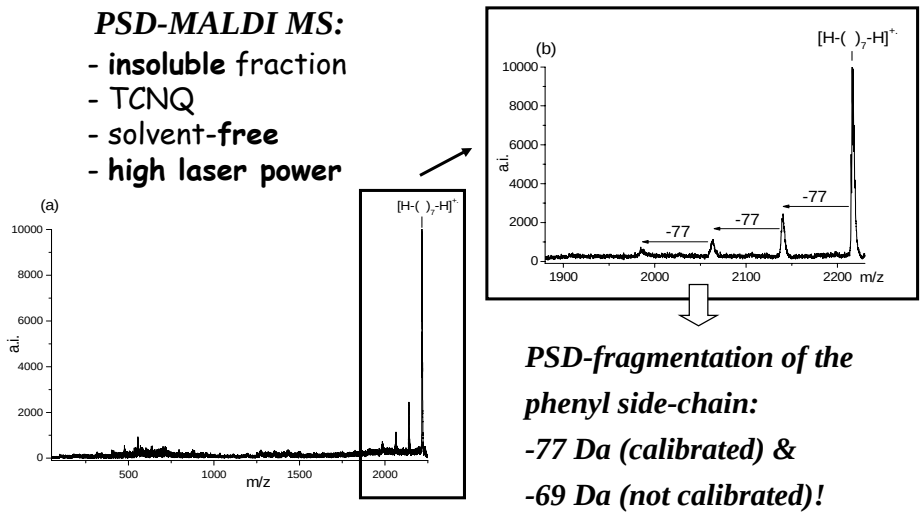
- TCNQ
- solvent-**free**



fragmentation of the phenyl side-chain:
ISD - 77 Da
PSD - 69 Da ?

Unequivocal Determination of ISD- and PSD-Fragmentation

PSD-MALDI MS:
- **insoluble** fraction
- TCNQ
- solvent-**free**
- **high laser power**



PSD-fragmentation of the phenyl side-chain:
-77 Da (calibrated) &
-69 Da (not calibrated)!

Outline

- Structure determination of monodisperse macromolecules
  - Phenylene dendrimers
  - Giant polycyclic aromatic hydrocarbons (PAH's)
- Structure determination of polydisperse macromolecules
  End group determination of homo-polymers
  - in simple cases (Poly(styrene))
  - in difficult cases (Poly(carbonate) and Poly(fluorene))
- Copolymers
  - PPE-b-PEO Diblock-copolymer
  - Random copolymers of amino acids

Traditional Copolymer Characterization:

- combinations of analytical methods (reactivity ratios, NMR)
- averaged properties of different chain lengths

MALDI-MS Copolymer Characterization:

- Allows *direct* information of
  Copolymer distribution and composition

Information about the primary structure?

- *„random"*- and *„block"*-polymer sequenz determination

→ ***MALDI-Fragmentation MS?***

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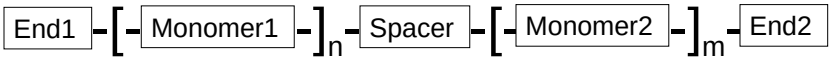
Composition of a diblock copolymer



Compositional information of resolved molecular weight distributions are not unequivocal

Interpretation of mass spectra often unclear due to signal overlapping caused by :

- unfavorable monomer masses e.g. $M_{Monomer1} \sim k \times M_{Monomer2}$
- low resolution due to high mass range or instrumental limitation

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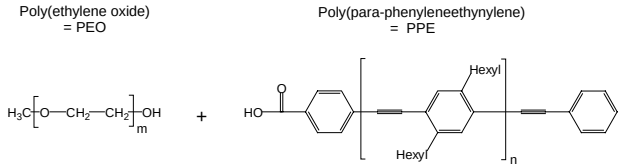
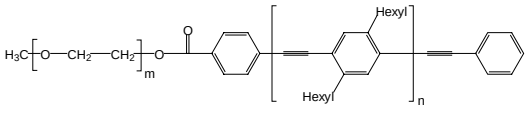
Formation of a PPE-*b*-PEO diblock copolymer

Poly(ethylene oxide) = PEO

Poly(para-phenyleneethynylene) = PPE



diblock copolymer synthesis



PEO-*b*-PPE

$M_{copo} = M_{End1} + m \times M_{Monomer1} + M_{Spacer} + n \times M_{Monomer2} + M_{End2}$

$= 15 + m \times 44 + 120 + n \times 268 + 101$

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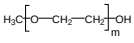
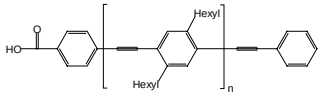
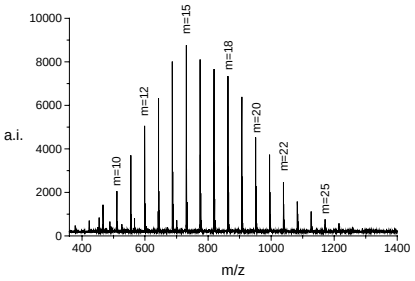
Composition of a PPE-*b*-PEO diblock copolymer

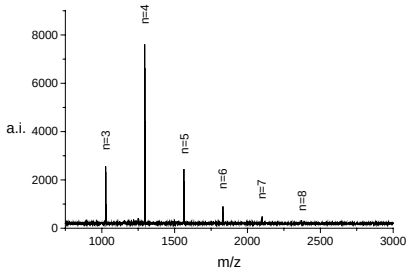
Investigation of each block, before reaction:







MALDI-TOF mass spectrum of PEO block



MALDI-TOF mass spectrum of PPE block

Agreement with expected PEO and PPE blocks

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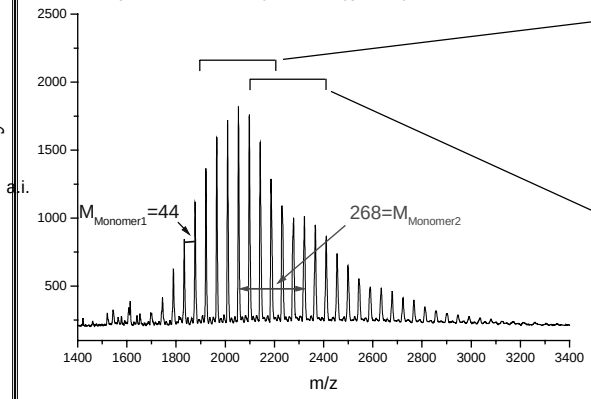
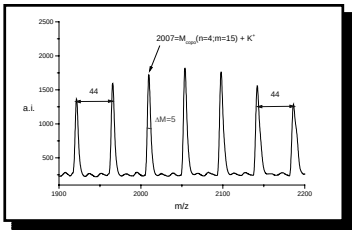
Composition of a PPE-b-PEO diblock copolymer

$M_{copo} = M_{End1} + m \times M_{Monomer1} + M_{Spacer} + n \times M_{Monomer2} + M_{End2}$

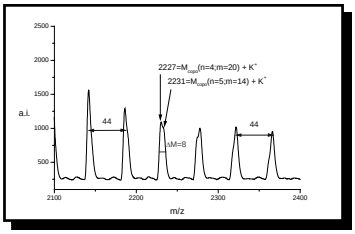
$= 15 + m \times 44 + 120 + n \times 268 + 101$



MALDI-TOF mass spectrum of PPE-*b*-PEO (low resolution)



pure signal



overlapping signals

Need of additional data → fragmentation of copolymer

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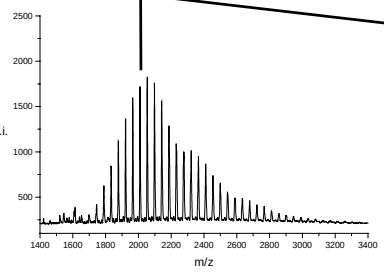
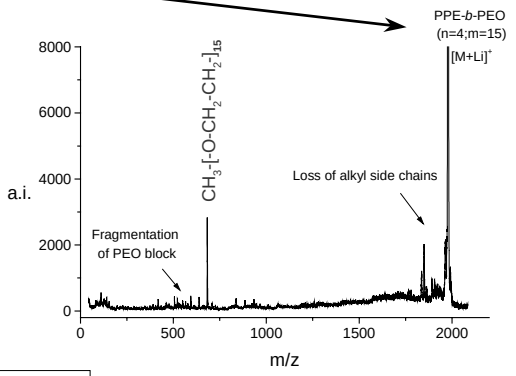
Composition of a PPE-b-PEO diblock copolymer

pure signal

selection and fragmentation



MALDI-TOF mass spectrum of PPE-*b*-PEO



Fragment mass spectrum

Most intense fragment peak ➔ Deduction of m, n

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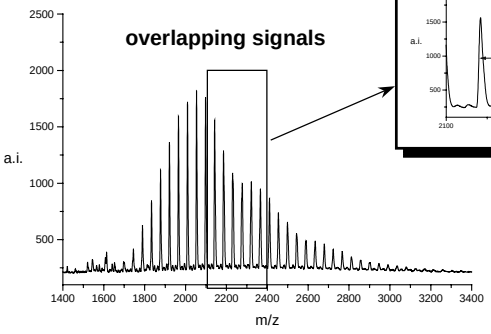
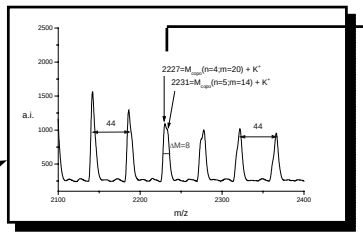
Composition of a PPE-b-PEO diblock copolymer

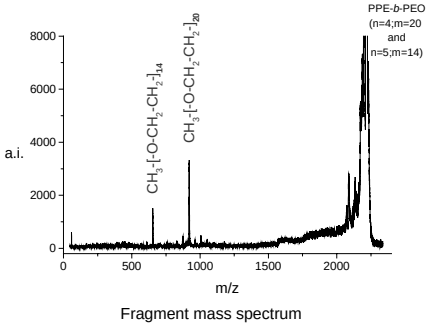
Information in case of superposition

overlapping signals





Selection and Fragmentation



Fragment mass spectrum

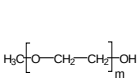
MALDI-TOF mass spectrum of PPE-*b*-PEO

Proof of 2 different structures !

Reconstruction of complete copolymer composition

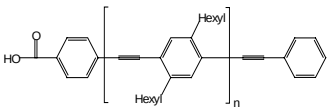
Copolymer Composition of
PPE-*b*-PEO diblock copolymer

Poly(ethylene oxide)
= PEO

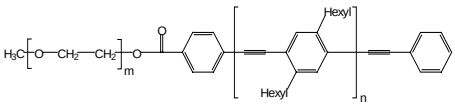


+

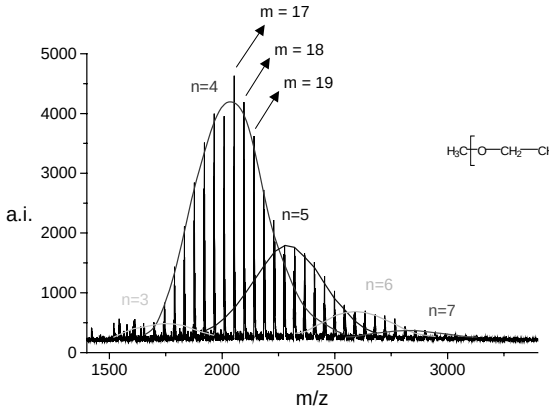
Poly(para-phenyleneethynylene)
= PPE



diblock copolymer synthesis

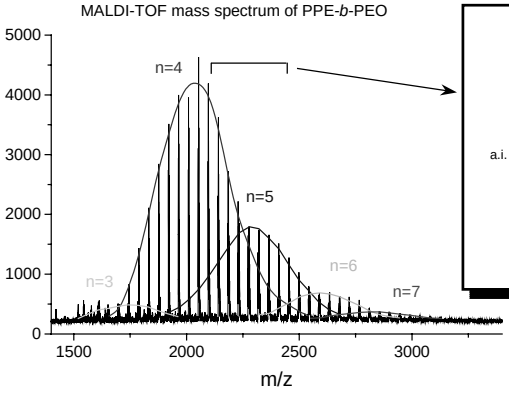


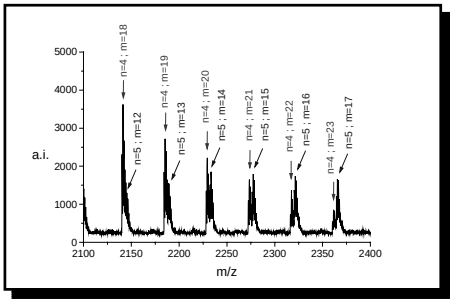
PEO*b*-PPE



Determination of Copolymer Composition at High Resolution

MALDI-TOF mass spectrum of PPE-*b*-PEO





Allows *direct* information on copolymer distribution and composition
by direct measurement of individual copolymer amounts due to resolved isotopic distributions

Sequence Determination of Synthetic Polymers

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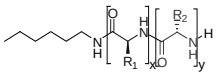
"Copolymer":

- *Monomer Units: 2*
- *Copolymer Types:*
  - *A B A B B A* *"random"*
  - *A A A B B B* *"block"*



- *amino acid monomer units*
- *no given primary structure*
- *polydisperse*
- *protected side-chains*

Characteristical structural elements of
natural polypeptides and industrial polymers

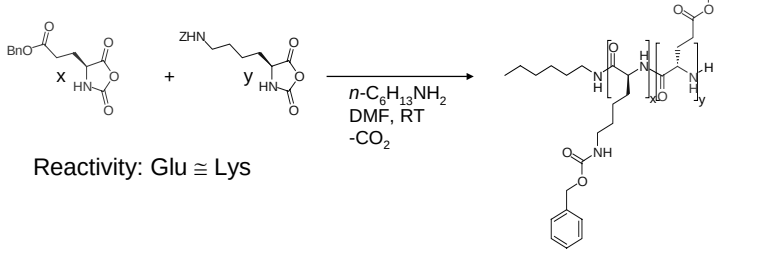
Synthetic Polypeptides

Max Planck Institute for Polymer Research

„Random" Copolymers:

n-Hex-NH-$(Glu)_x$-*st*-$(Lys)_y$-H

Glu Lys



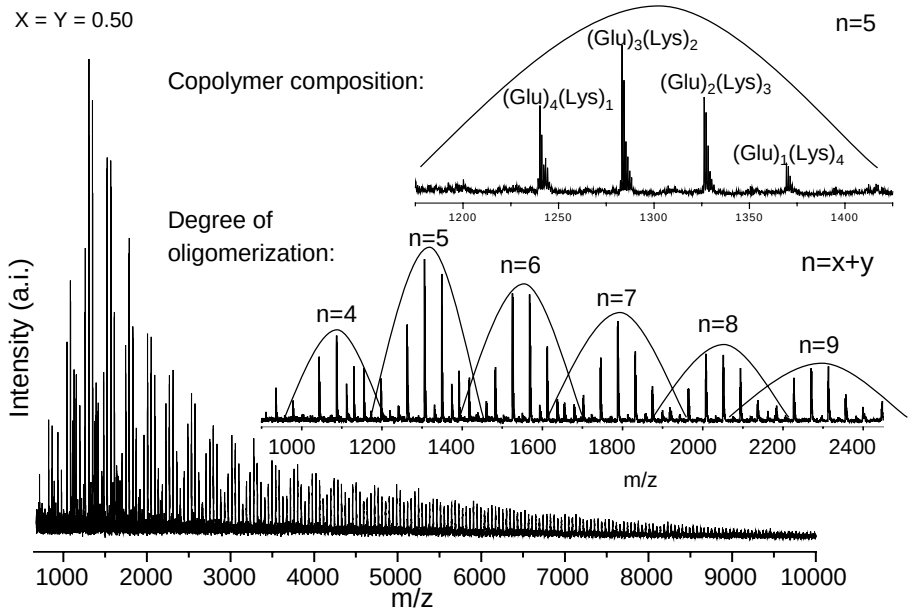
Reactivity: Glu ≅ Lys

Block-Copolymers:

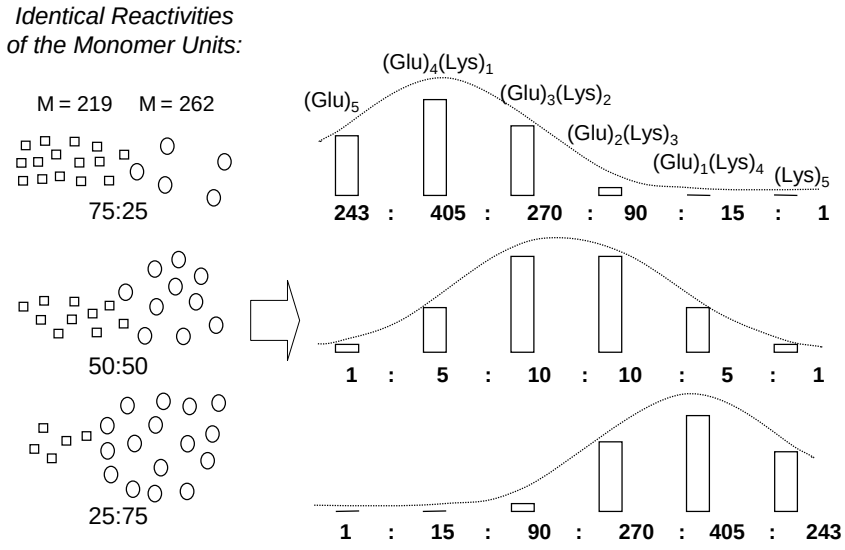
n-Hex-NH-$(Glu)_x$-*bl*-$(Lys)_y$-H

n-Hex-NH-$(Lys)_y$-*bl*-$(Glu)_x$-H

MALDI-TOF of „Random“ n-Hex-NH-$(Glu)_x$-*st*-$(Lys)_y$-H



Theory of Probabilities: Monitoring with MALDI MS?



MALDI-TOF of „Random“ Pentamers

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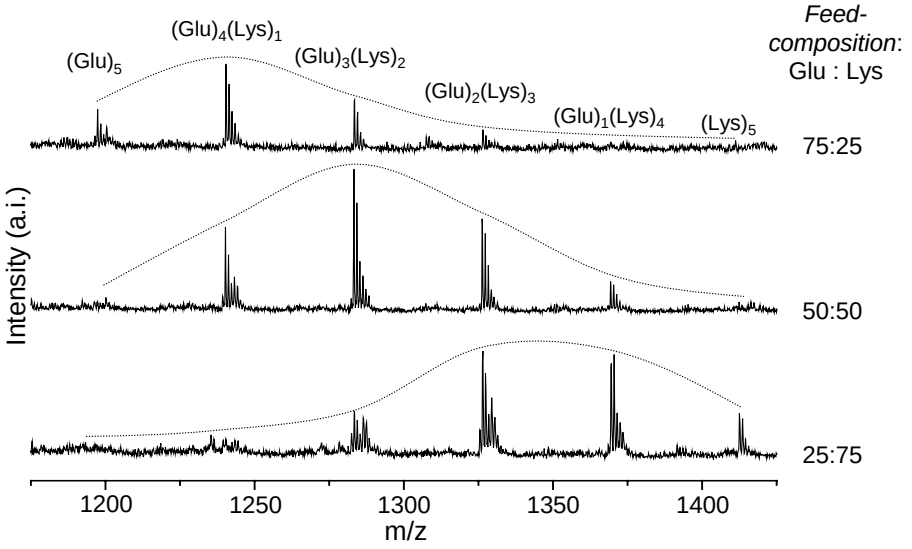

Theory of Probabilities for Sequenz Composition

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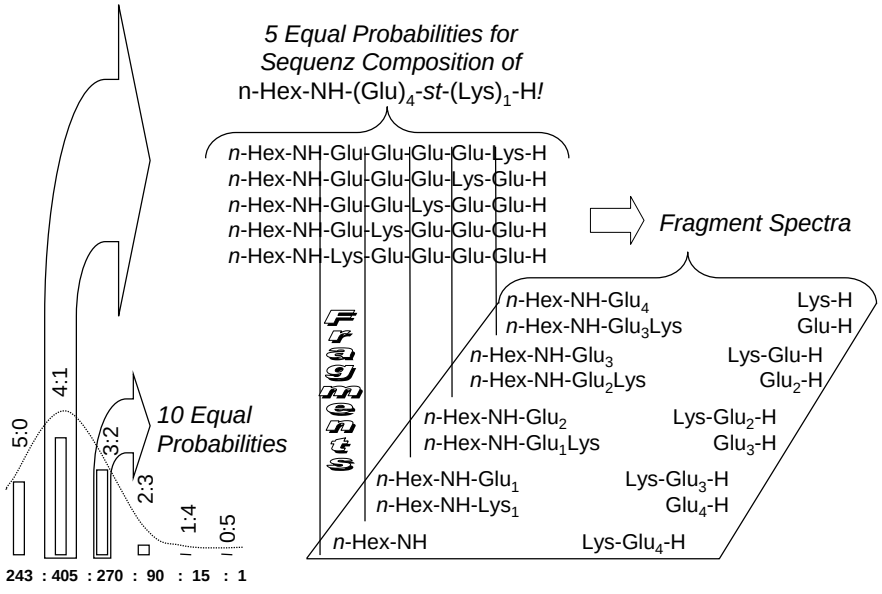

PSD Fragment Ion-Analysis of a „Random“ Pentamer

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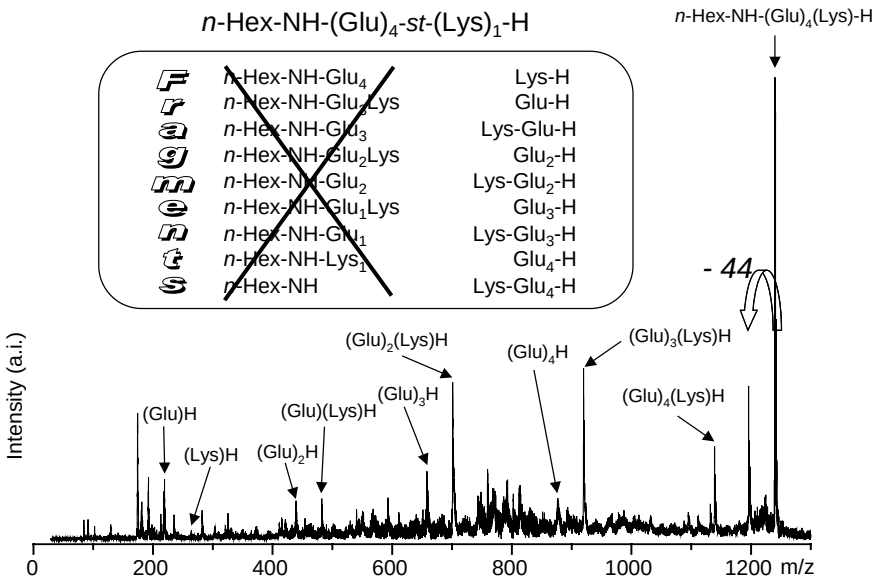

Sequenz analysis of a Block-Copeptid

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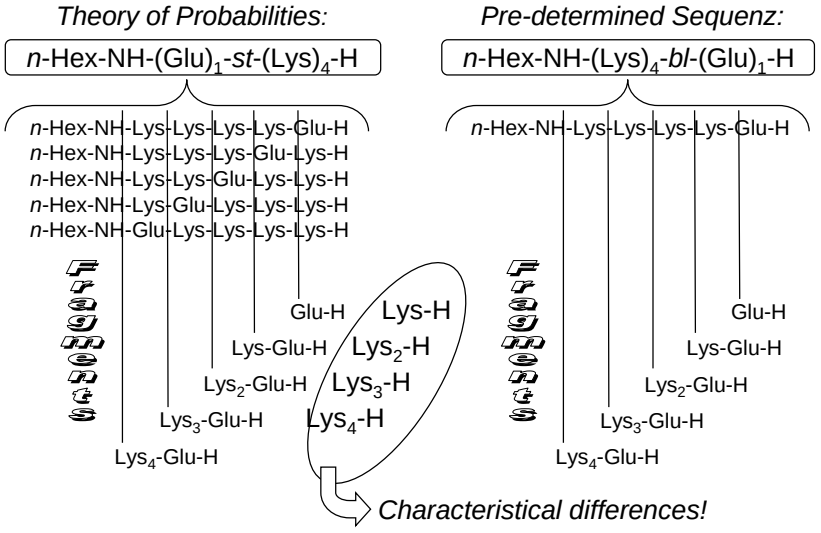

Sequenz Analysis of a "Block"-Copolymer

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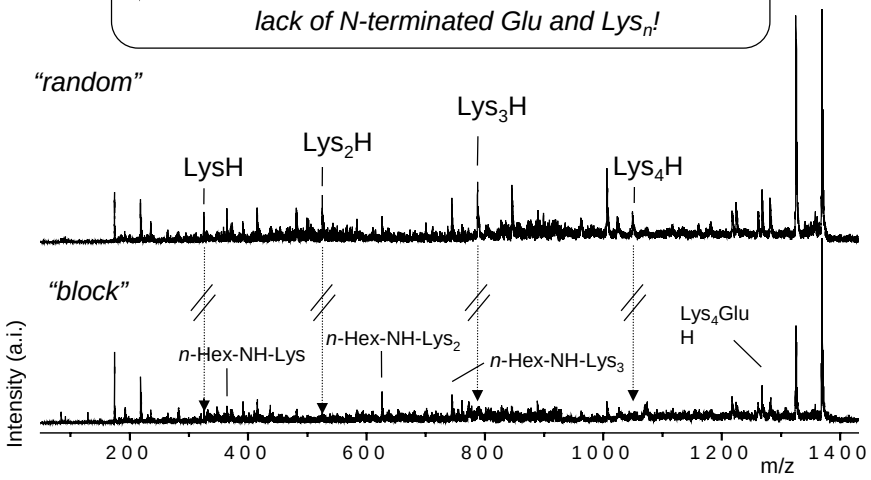
n-Hex-NH-Lys-Lys-Lys-Lys-Glu-H

Characteristical differences for the „block" peptide: lack of N-terminated Glu and Lys_n!



Qualitative Interpretation of Fragmentation

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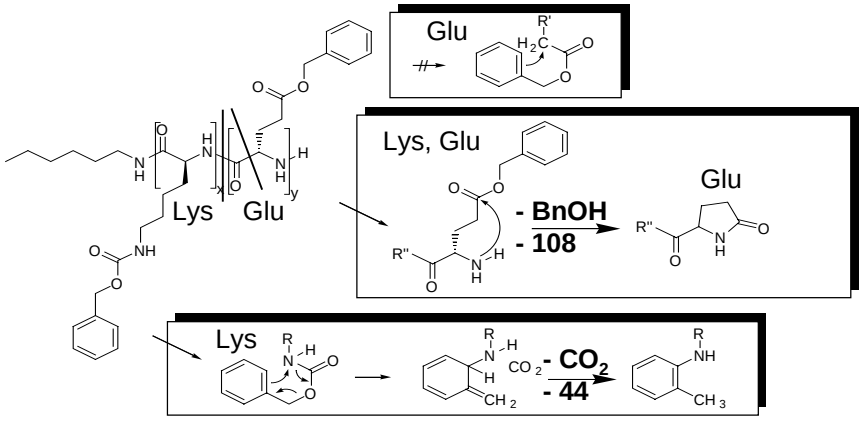
- 44 fragments
-108 fragments:
C-terminated fragments
- 28 fragments

Lys: McLafferty rearrangement
Lys, Glu: Aminolysis
Lys
Glu: different backbone cleveage



Acknowledgement

Max Planck Institute for Polymer Research

Coworkers

Laurence Przybilla [1]

Sarah Trimpin

Sabine Kummer

Kai Martin

Kimihiro Yoshimura

Jochen Spickermann

Ali Pouhanipour

Stefan Türk