



## HPLC-MALDI-TOF Mass Spectrometry for the Analysis of Complex Polymers

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Das DKI ist eine Einrichtung der Forschungsgesellschaft Kunststoffe e.V., Mitglied der

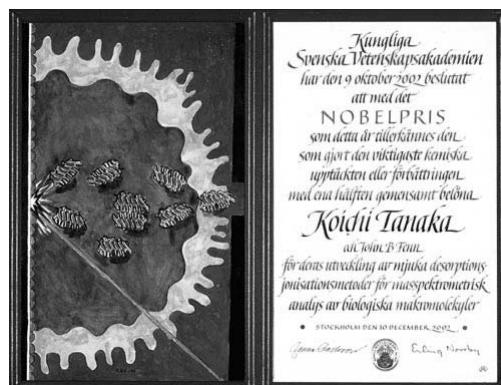


## Shimadzu's Scientist Koichi Tanaka Received Nobel Prize in Chemistry 2002

On December 10<sup>th</sup>, 2002, Nobel Prize Award Ceremony took place in Stockholm, Sweden. Koichi Tanaka, fellow of Shimadzu Corporation, received his Nobel medal and diploma in Chemistry from his Majesty the King of Sweden, King Carl XVI Gustaf.

Tanaka received the prize for the development of soft desorption ionization methods for mass spectrometric analyses of biological macromolecules to identify and reveal the structures of such molecules.

Tanaka is the 12th Japanese citizen who has received a Nobel Prize.

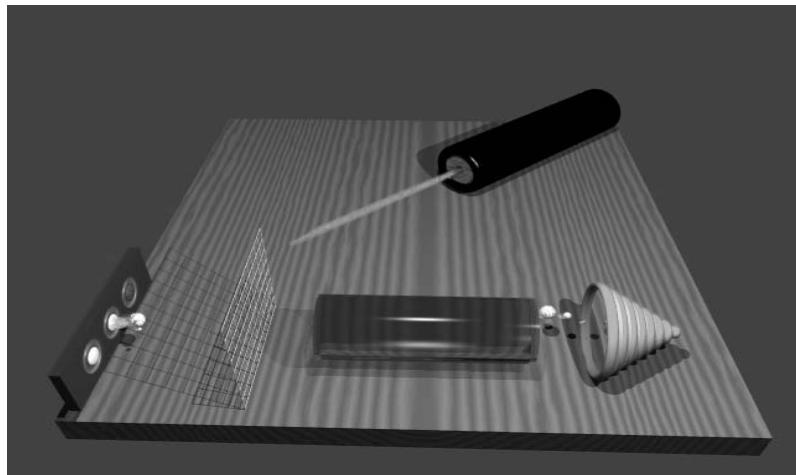


## Why Coupling of LC and MALDI-TOF MS ?

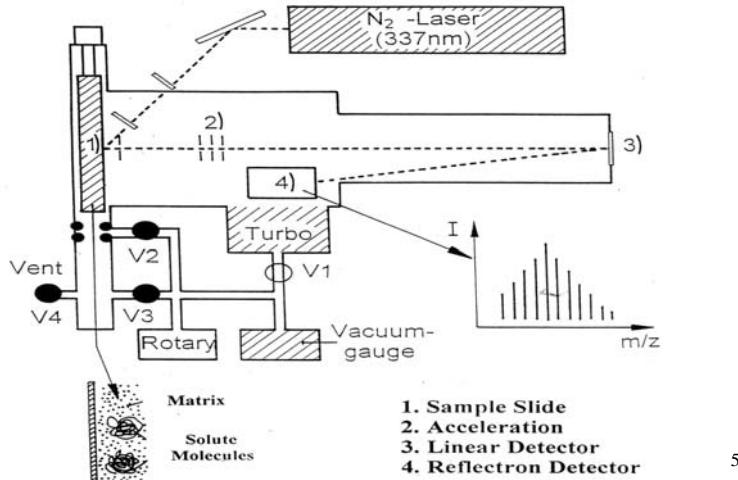
- Samples with high polydispersity ( $M_w/M_n > 1,2$ )
- GPC calibration without calibration standards
- Analysis of complex polymers  
multiple distributions: FTD-MMD, CCD-MMD
- Determination of small amounts of by-products
- „High-throughput“ analysis for combinatorial materials research

3

## Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry



## Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry



## Principle Ideas of MALDI-TOF MS

- upon laser irradiation all molecules obtain similar energies

$$E_{\text{kin}} = 0.5 m v^2$$

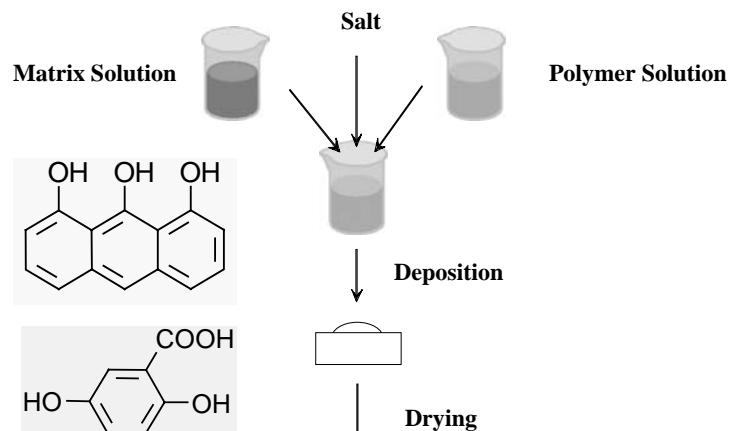
⇒ at similar kinetic energies: molecules of different masses have different flight velocities  
(higher  $m$  means lower  $v$ )

- flight time in the TOF mass analyzer

$$T \sim L (m/z U)^{0.5}$$

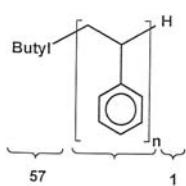
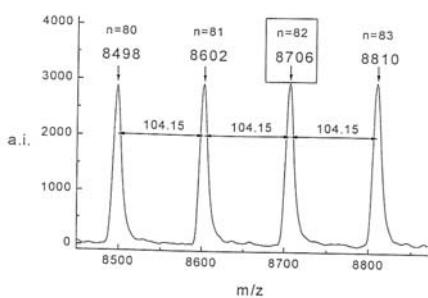
T - ion flight time, L - length of drift tube,  
m - ion mass, z - ion charge, U - acceleration voltage

## Sample Preparation for MALDI-TOF MS

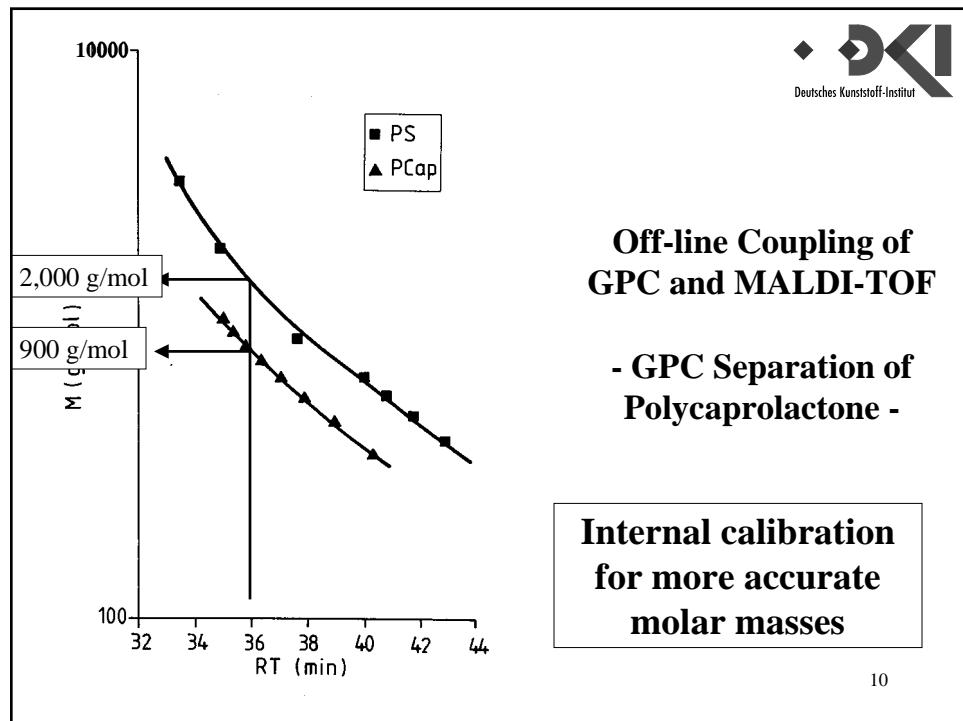
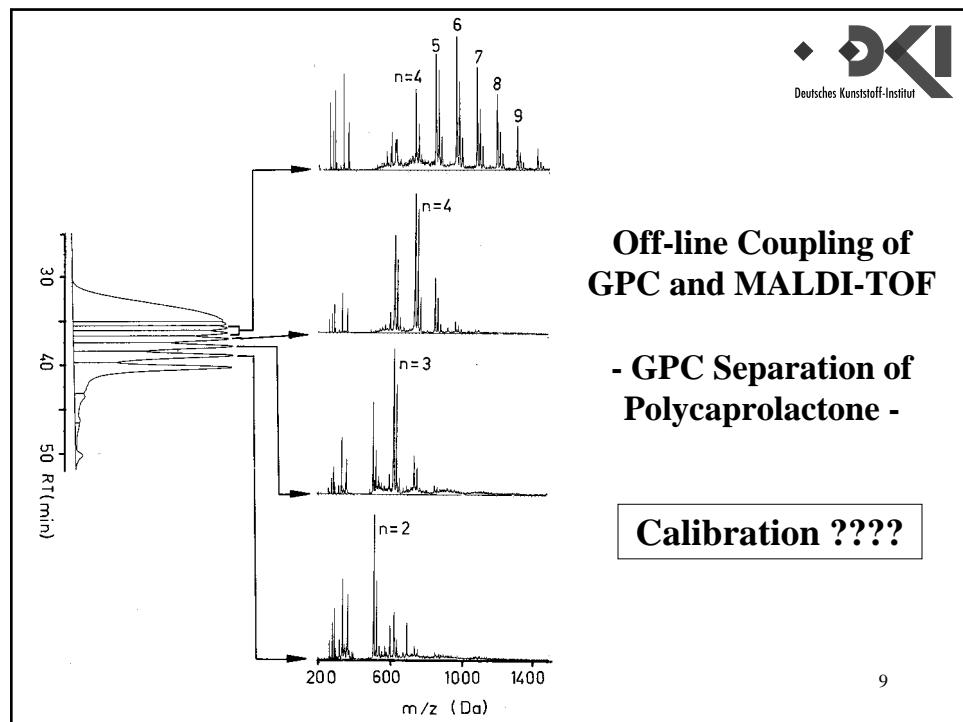


7

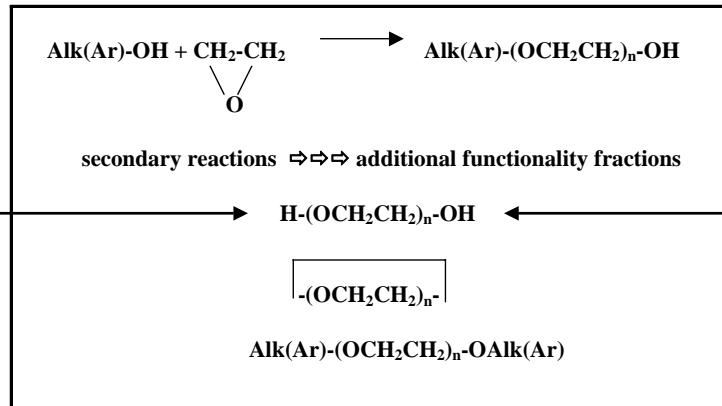
### Interpretation of a MALDI-TOF Spectrum -Anionically polymerized polystyrene-



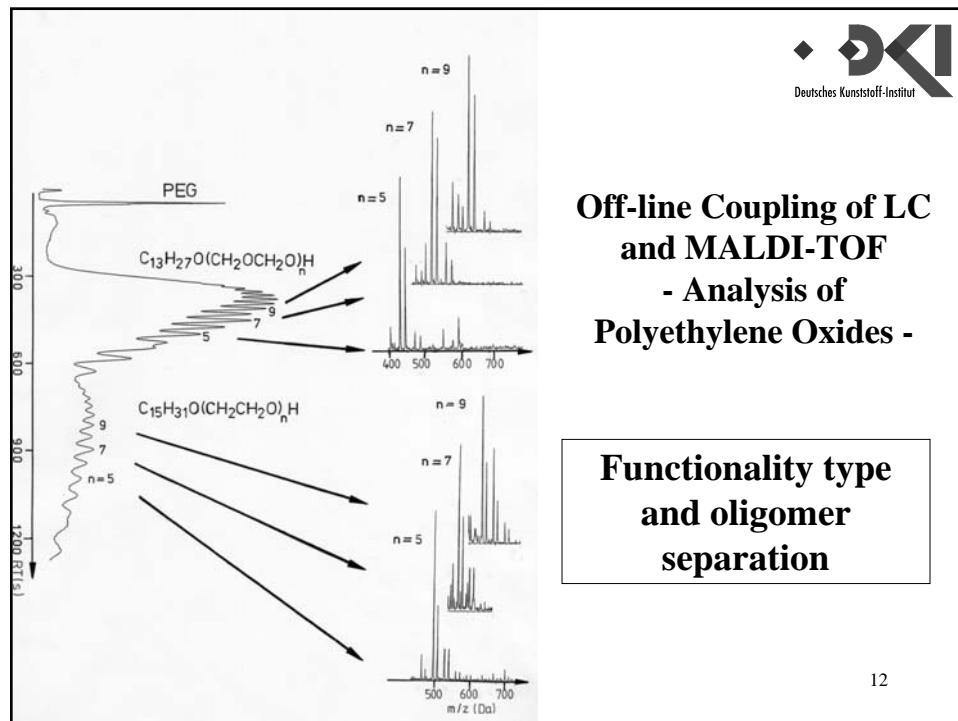
$$8706 = 82(n) \times 104.15 \text{ (Styrene)} + 57 \text{ (Butyl)} + 1 \text{ (Hydrogen)} + 108 \text{ (Ag}^+)$$



## Off-line Coupling of LC and MALDI-TOF - Analysis of Polyethylene Oxides -



11

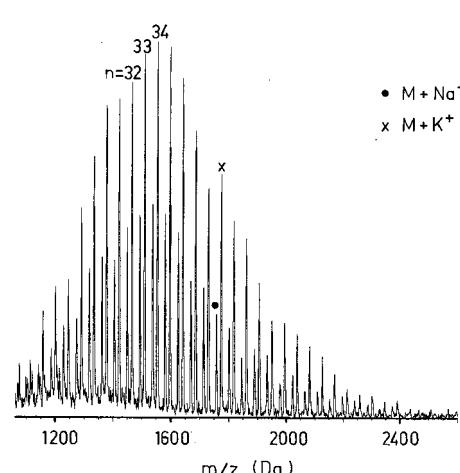


12

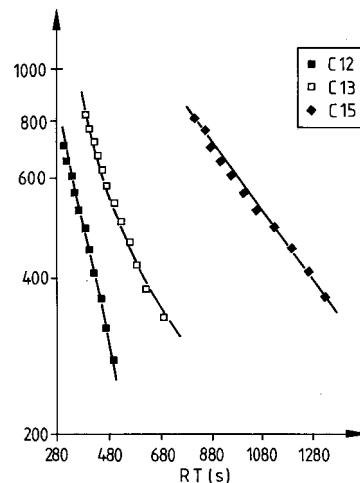
**Off-line Coupling of LC and MALDI-TOF**  
**- Analysis of Polyethylene Oxides -**



Deutsches Kunststoff-Institut

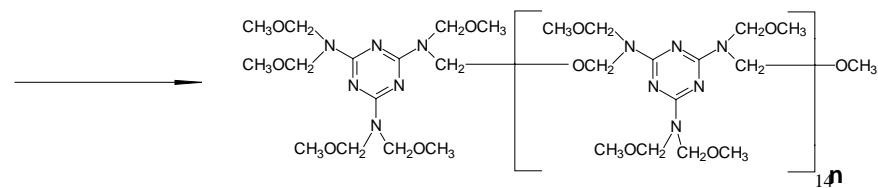
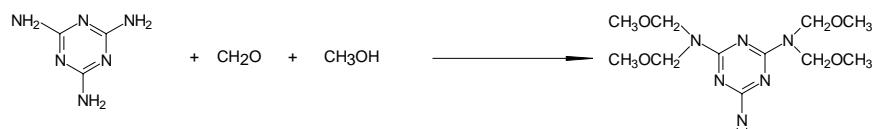


Spectrum of fraction 1

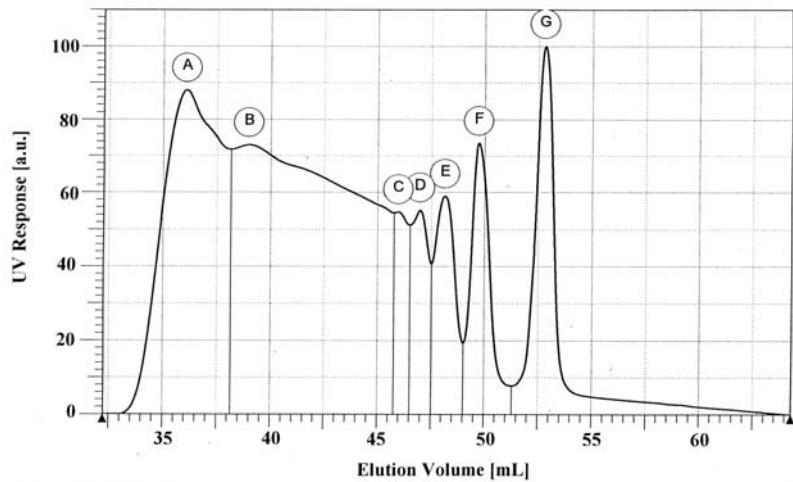


GPC calibration of functionality fractions

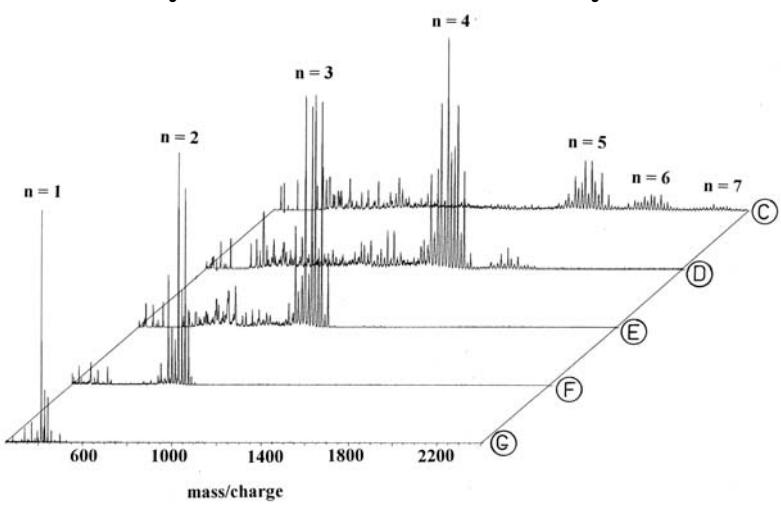
**Analysis of Methoxylated Melamine-Formaldehyde Resins**



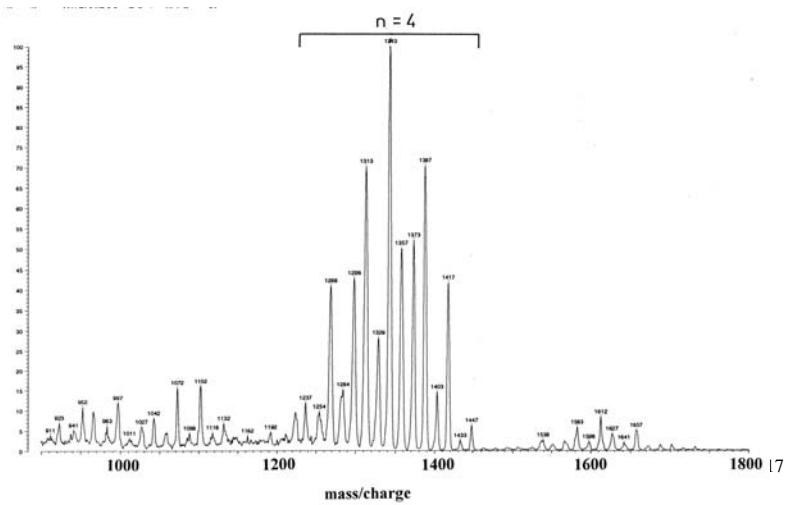
### GPC of a Methoxylated Melamine-Formaldehyde Resin



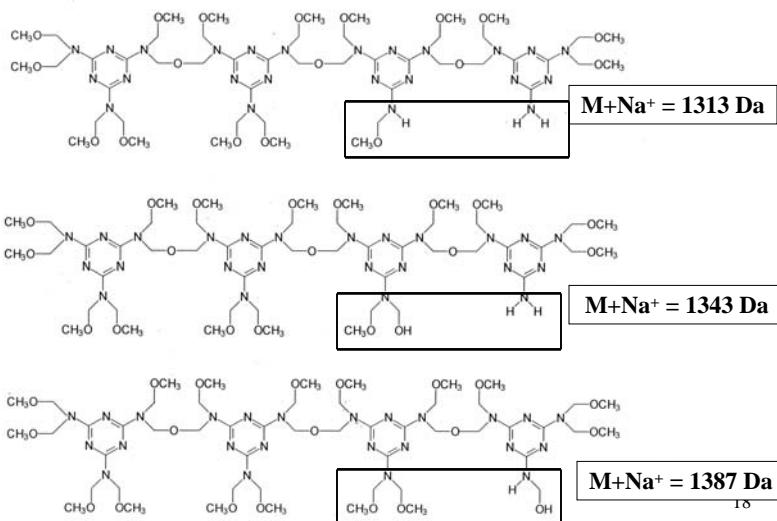
### MALDI-TOF Spectra of GPC Fractions of a Methoxylated Melamine-Formaldehyde Resin



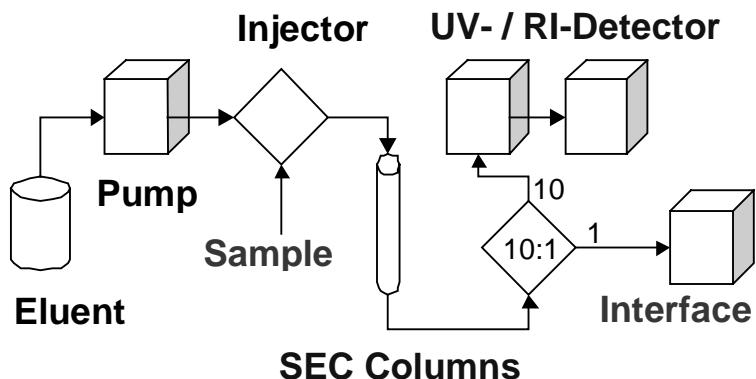
## Enlarged Tetramer Region of the MALDI-TOF Spectrum



## Chemical Structures of the Tetramers

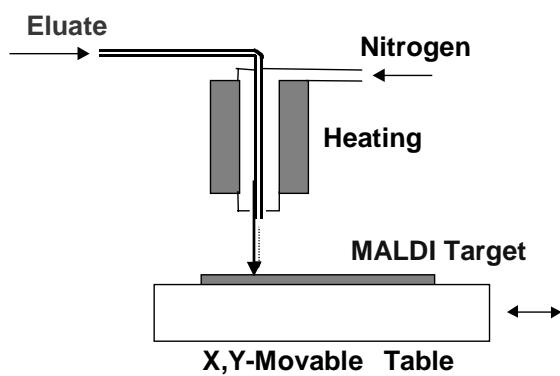


## On-line Coupled GPC/MALDI-TOF MS



19

## Schematic Presentation of a LC/MALDI-TOF Interface (Lab Connections)



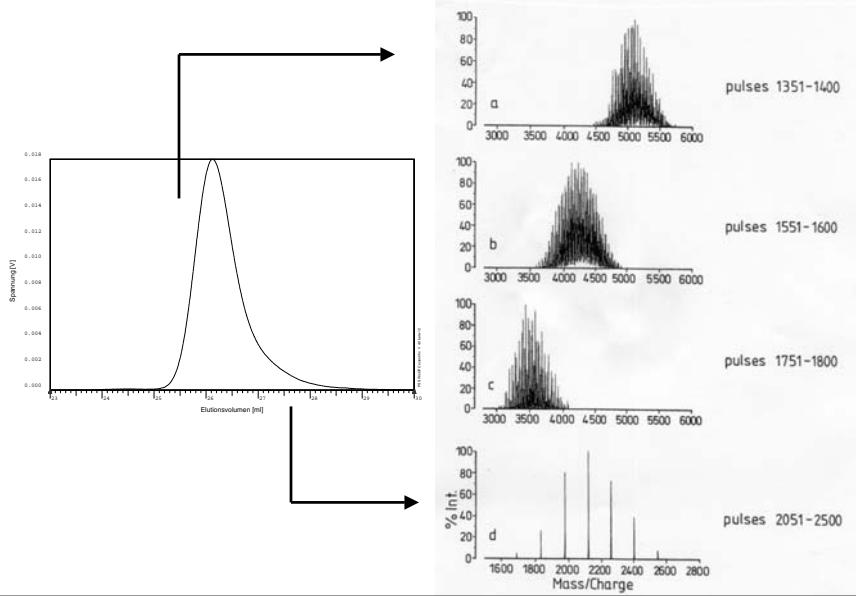
20

## Lab Connections LC/MALDI-TOF Interface Model 600 and Pre-coated MALDI Targets

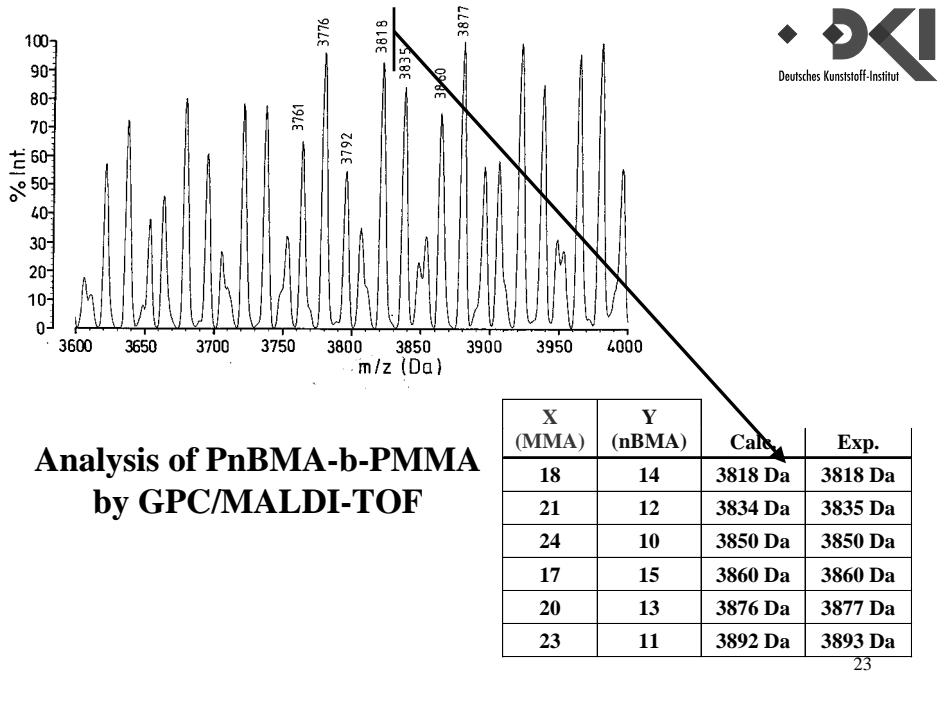


21

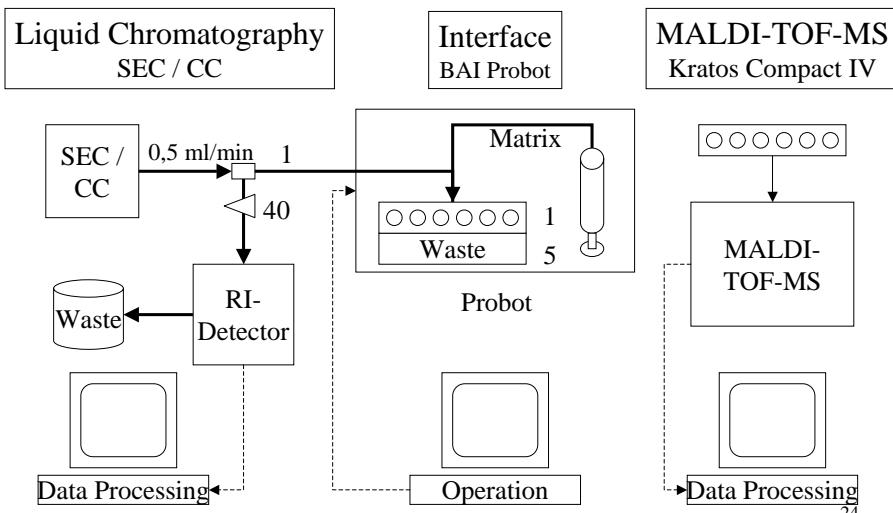
### Analysis of PnBMA-b-PMMA by GPC/MALDI-TOF



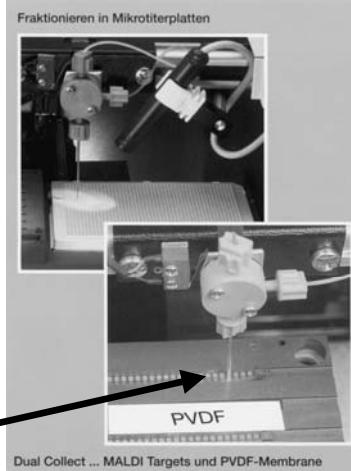
22



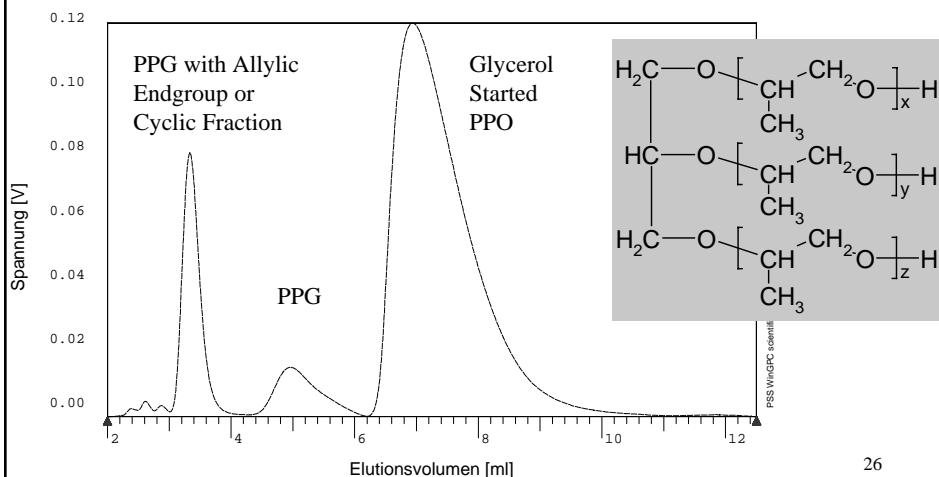
### LC/MALDI-TOF Interface (BAI)



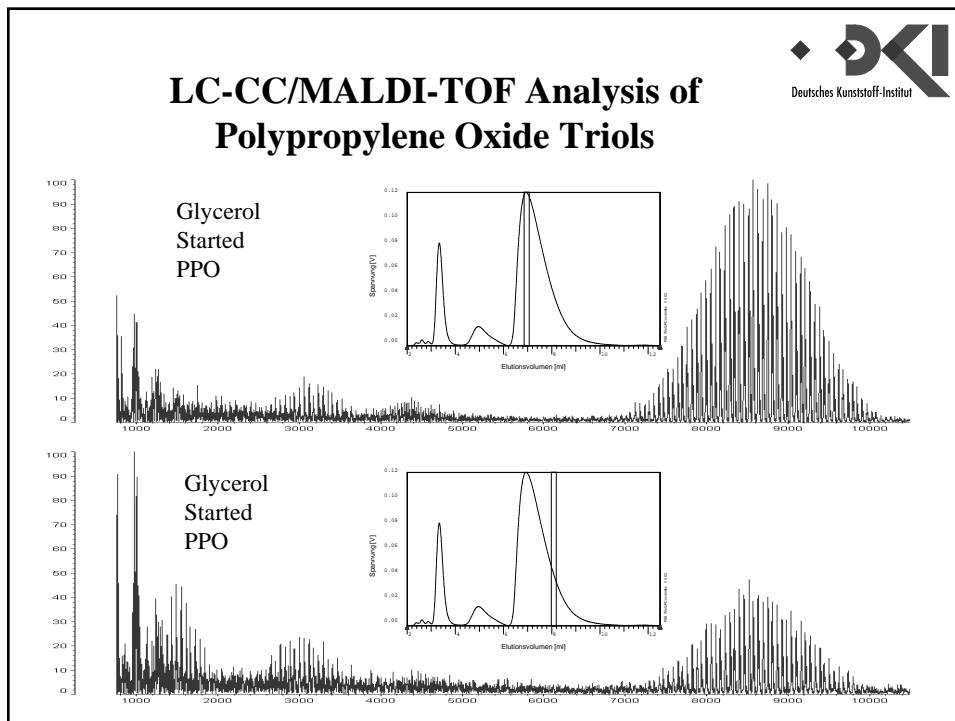
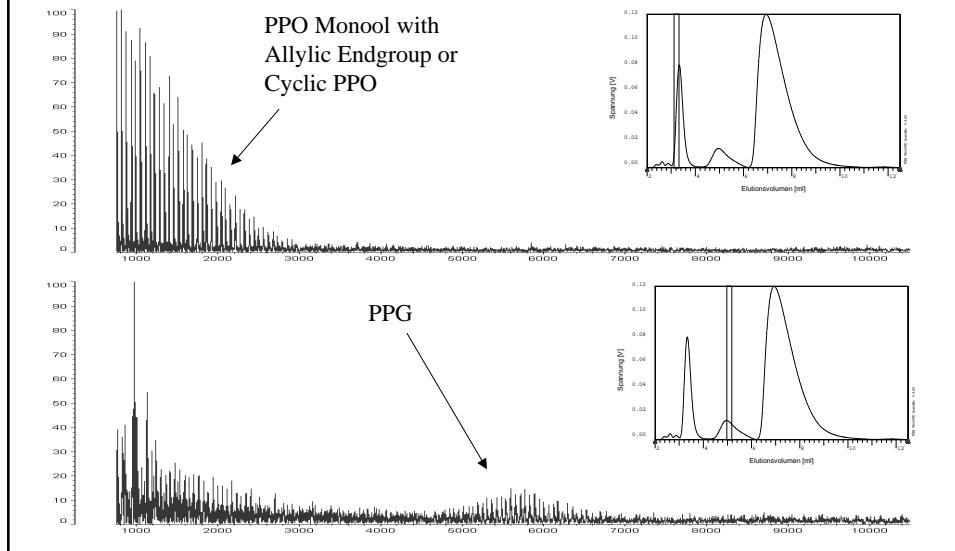
## LC/MALDI-TOF Interface PROBOT (BAI)



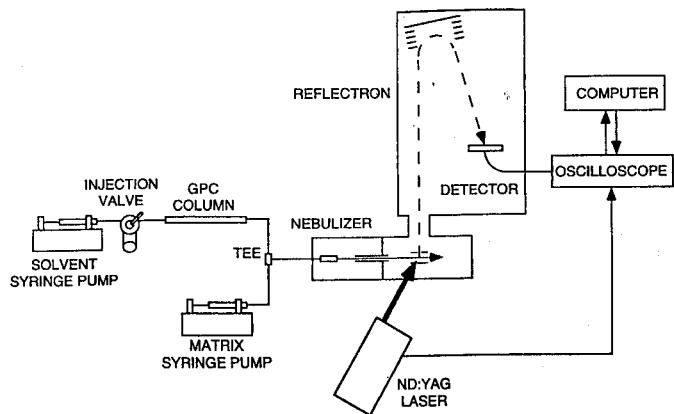
## LC-CC/MALDI-TOF Analysis of Polypropylene Oxide Triols



## LC-CC/MALDI-TOF Analysis of Polypropylene Oxide Triols



## Direct Coupling of LC and MALDI-TOF MS

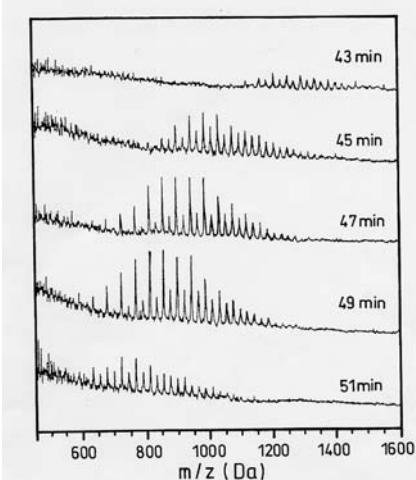


**Aerosol MALDI-TOF instrument coupled to GPC**

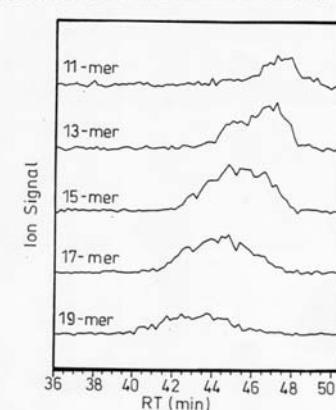
X. Fei, K.K. Murray, Anal. Chem. 68 (1996) 3555

29

## Direct Coupling of LC and MALDI-TOF MS

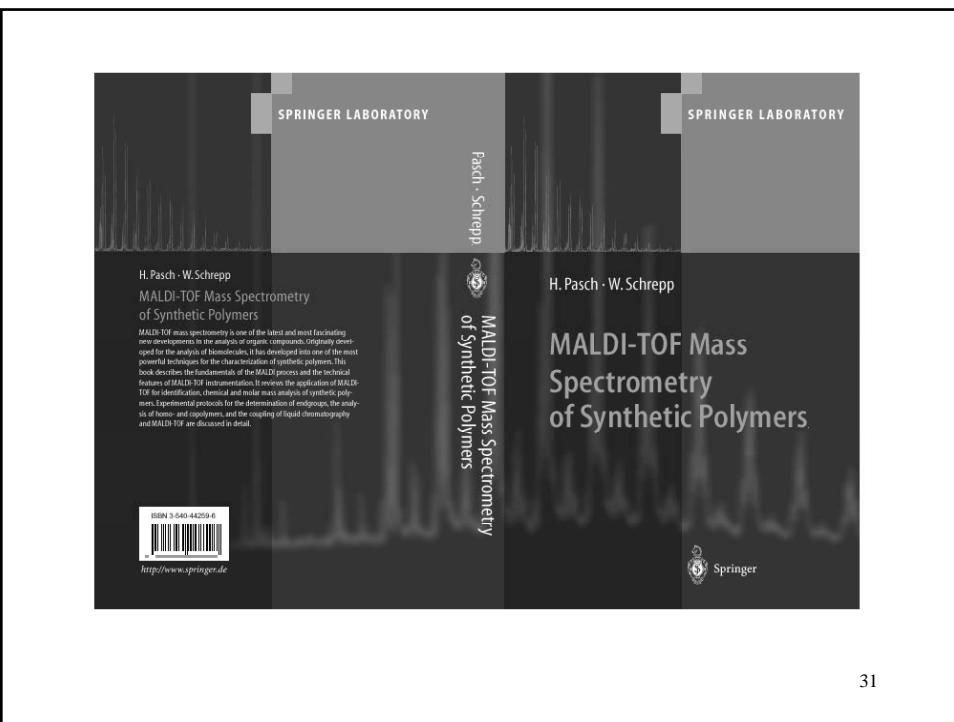


**Spectra of fractions**



**Single ion chromatograms**

30



31