ThP 446: Rapid fingerprinting of high-molecular-weight polymers containing C-O, Si-O or C-S bonds by Desorption Ionization Using Through-Hole Alumina Membranes

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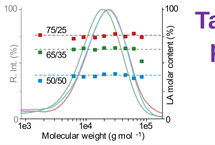
Direct application:
SEC-DIUTHAME-MS for **high-molecular-weight PLGA**



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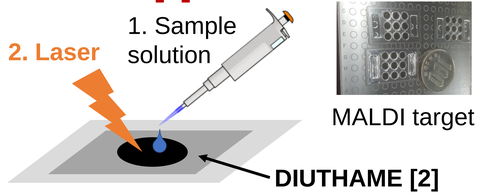
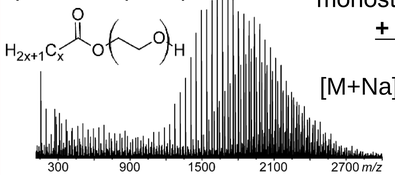
Rationale [1]



MALDI target

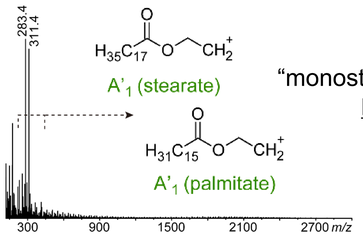
Stearate (x=17)
palmitate (x=15)



■ PEG "monostearate" **+ NaTFA**

$[M+Na]^+$

→ Intact polymer peak series = **SALDI-MS**



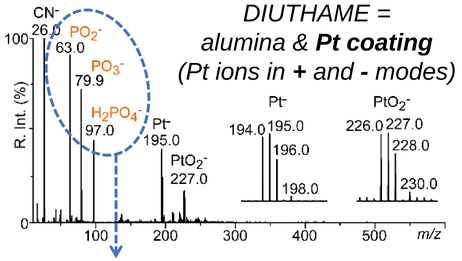
■ PEG "monostearate" **No salt**

→ Fragment ions = **"reactive" SALDI-MS**

In-source protonation / dissociation induced by DIUTHAME [3]

Fragment ions in **DIUTHAME-MS** of PEOs with no salt ~ product ions of protonated PEOs in **ESI-MS/MS** ($[M+H]^+$ or $[M+NH_4]^+$

DIUTHAME mass spectrum of an **empty spot**, negative ion mode



*DIUTHAME = alumina & **Pt coating** (Pt ions in **+** and **-** modes)*

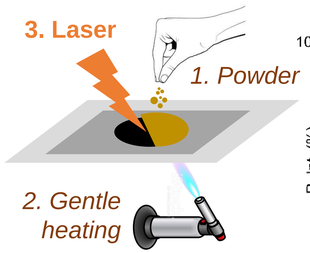
Traces of phosphoric acid remaining in the through-holes released upon laser pulses

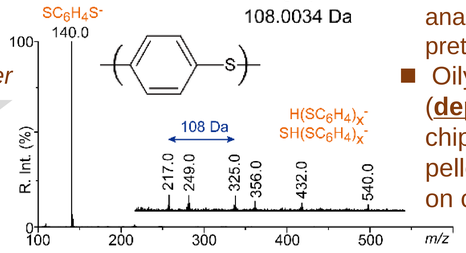
Reasonable origin of in-source protonation

→ Protonated polymer chains **rapidly dissociate in-source** ~ MS/MS fingerprint
→ **Pt ions** used as **internal calibrant**

"solvent-free DIUTHAME" for insoluble sample [3]

Example: PPS, **DIUTHAME**

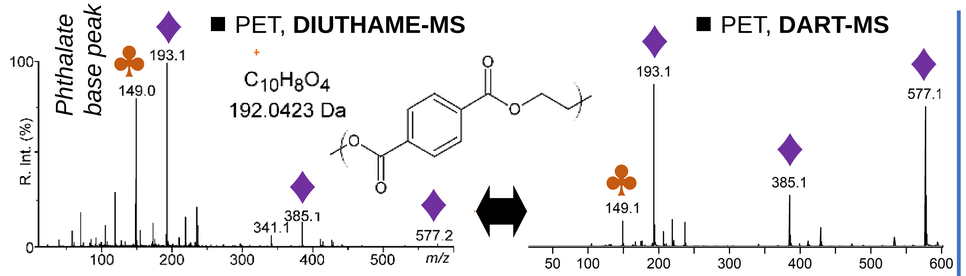




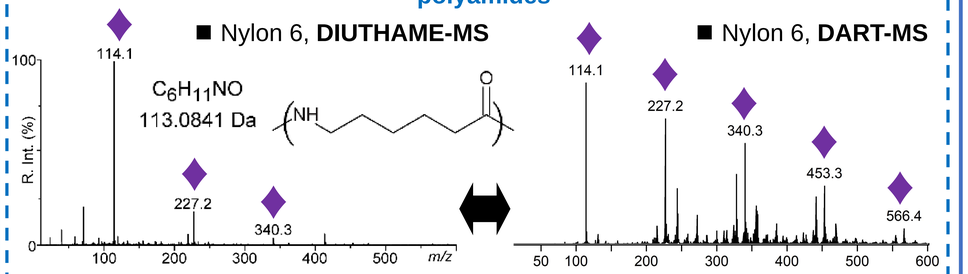
- Insoluble samples analyzed without pretreatment
- Oily polymers (**deposited** on chip), powder & pellets (**melted** on chip)

Application to high-molecular-weight polymers of various classes [3]

- High-molecular-weight and/or high dispersity = no signal in MALDI-MS
- "Reactive" SALDI using DIUTHAME: in-source protonation/dissociation of polymer chains with cleavable bonds (e.g. ester, amide, siloxane…) regardless of the molecular weight → **rapid fingerprinting with two main types of fingerprint**

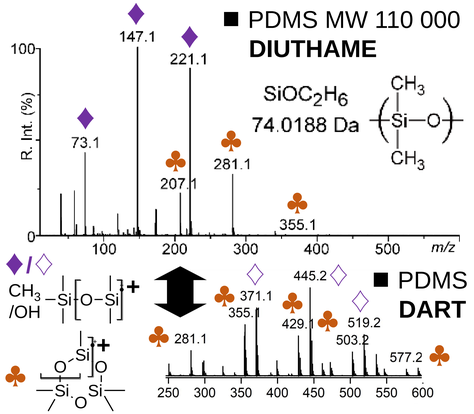


polyamides



■ Distinction of monadic/dyadic nylons
■ Chain length of the **amine block**

Other **nylons, phenoxy resins, copoly-ethers, copoly-esters**

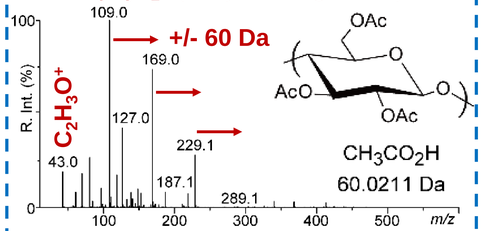


→ Mainly **protonated monomers** ($[M_n + H]^+$ peak series, ♦)

Functionalized celluloses (MW>200 000)

■ Cellulose triacetate, **DIUTHAME-MS**

$C_6H_5O_2^+$ (dehydrated glucose)



■ **Functionalization** highlighted by mass differences of product ions
■ Distinction of celluloses triacetate, propionate and acetate/butyrate

→ Mainly **fragment ions**

→ **"Reactive" SALDI fingerprint by DIUTHAME similar to DART-MS, supporting the hypothesis of in-source protonation**

References: [1] *Rapid Commun. Mass Spectrom.* **2020**, *34*, e8597; [2] *Rapid Commun. Mass Spectrom.* **2018**, *32*, 1851; [3] *Anal. Chem.*, under review.