MS Analysis of Synthetic Polymers

Mass Spectrometry Reviews, **1999**, *18*, 309-344

Typical Properties Measured

- Molecular Weight Distribution
  - M_n - Number Average
  - M_w - Weight Average
  - P_d - Polydispersity
- Repeat Unit Mass
  - Repeat Unit Molecular Formula
- End Group Mass
  - End Group Molecular Formula

Ionization Techniques

- MALDI
  - Typically singly charged ions
  - Matrix Selection can be difficult
  - Cationization agent is important
- ESI
  - Distribution of charge states
    - complicates spectrum when combined with weight distribution
  - Solubility/Polarity Limitations

Mass Analyzers

- TOF
  - High mass range is necessary for analysis of large polymers by MALDI
- FTMS
  - High resolution can allow analysis of complicated ESI polymer spectra
- QTOF
  - For moderately high (20 kDa) MALDI-MS
    - more accurate than standard TOF

MALDI-TOF

- Both IR and UV lasers have been used
  - UV is more common (337 nm N_2 Laser)
- Matrix Selection
  - Matrix should absorb at 337 nm
  - Match hydrophobic/hydrophilic character of matrix/sample
- Cationization
  - Cation should bind to polymer functional group
- Sample Preparation
  - Inhomogeneous samples make automation difficult

UV Matrices

Hydrophilic

DHB	Polypropylene glycol
CCA	Polyvinyl acetate
Ferulic Acid	Polytetramethylene glycol
IAA	Polymethylmethacrylate
Dithranol	Polystyrene
trans-Retinoic acid	Polybutadiene
Diphenylbutadiene	Polydimethylsiloxane

Hydrophobic

Cationization

- Polar polymers (ethers, esters, etc) can be ionized by alkali metals
  - Small impurities can be enough to cause unintentional cationization
  - Addition of Na, K can simplify spectrum
- Nonpolar polymers can be cationized by metals that bind to pi systems
  - Ag and Cu with polystyrene polyisoprene etc.
- Saturated polymers are difficult
  - polyethylene, polypropylene require derivatization or other techniques (FD)

Sample Preparation

- Optimally, a mixture of polymer, matrix, and salt in a single solvent
  - At least ~1000 fold molar excess of matrix
  - ~2-5:1 salt:polymer ratio
- Dried droplet
  - 1µL of mixture is applied to target
    - fast drying can improve reproducibility
- Electrospray deposition
  - vastly improved homogeneity
- Solventless Grinding
  - mixing dry components with magnetic BBs

Mass Discrimination

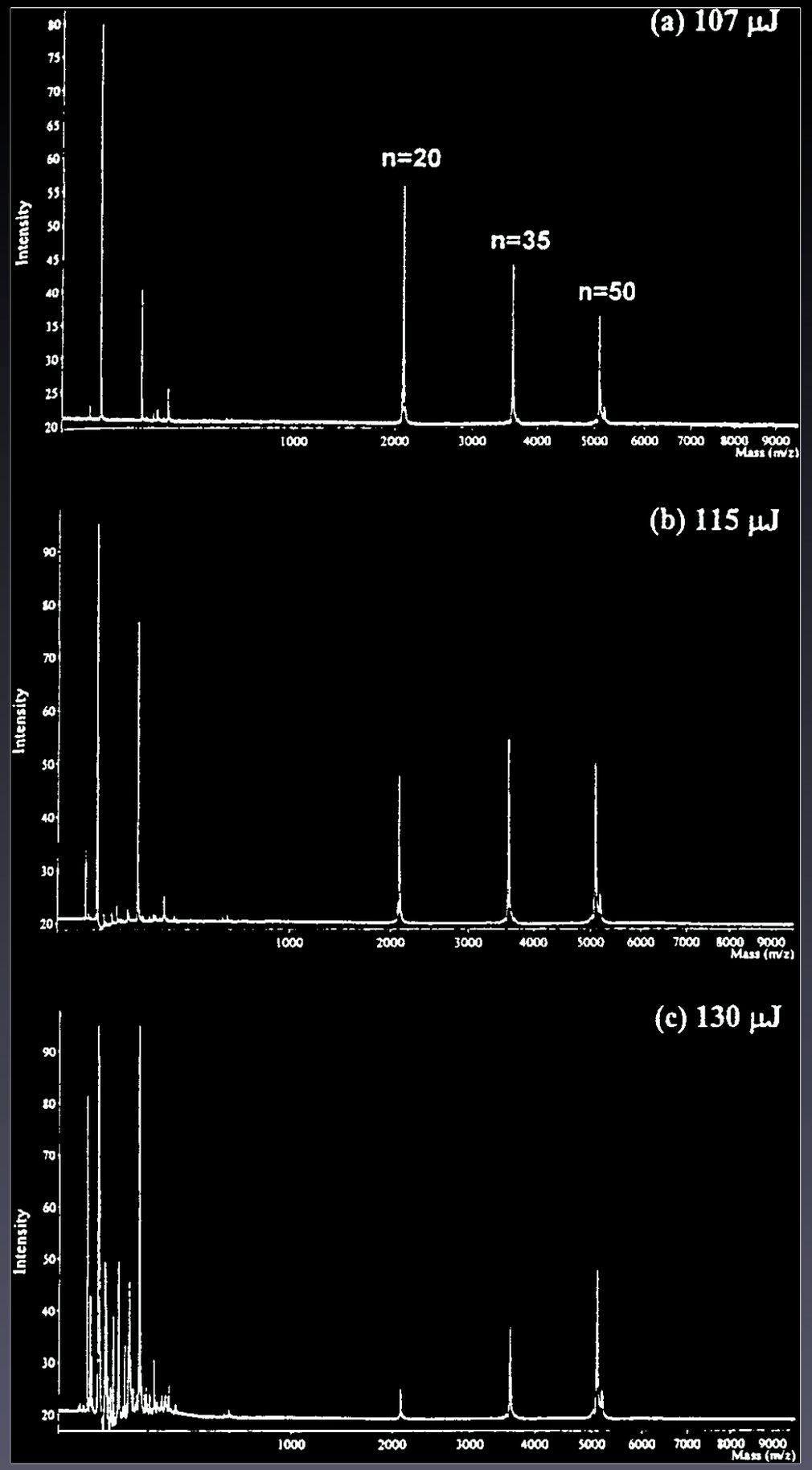
- Sources of Mass Discrimination
  - Sample Preparation/Crystallization
  - Desorption/Ionization/Cationization
  - Ion Transmission
  - Ion Detection
- Polymers of P_d>1.2 could give inaccurate molecular weight distributions
- Separations (SEC, GPC) coupled to MS can give accurate measurement for polydisperse samples

Mass Discrimination

- Polymer may fractionate upon co-crystallization with matrix
  - Electrospray deposition can minimize this
- Choice of cation can affect measured distribution
  - Different chain lengths can prefer differently sized cations
- MCP detector can discriminate against higher masses in the presence of lower
  - other detector designs can mediate this, but resolution is compromised

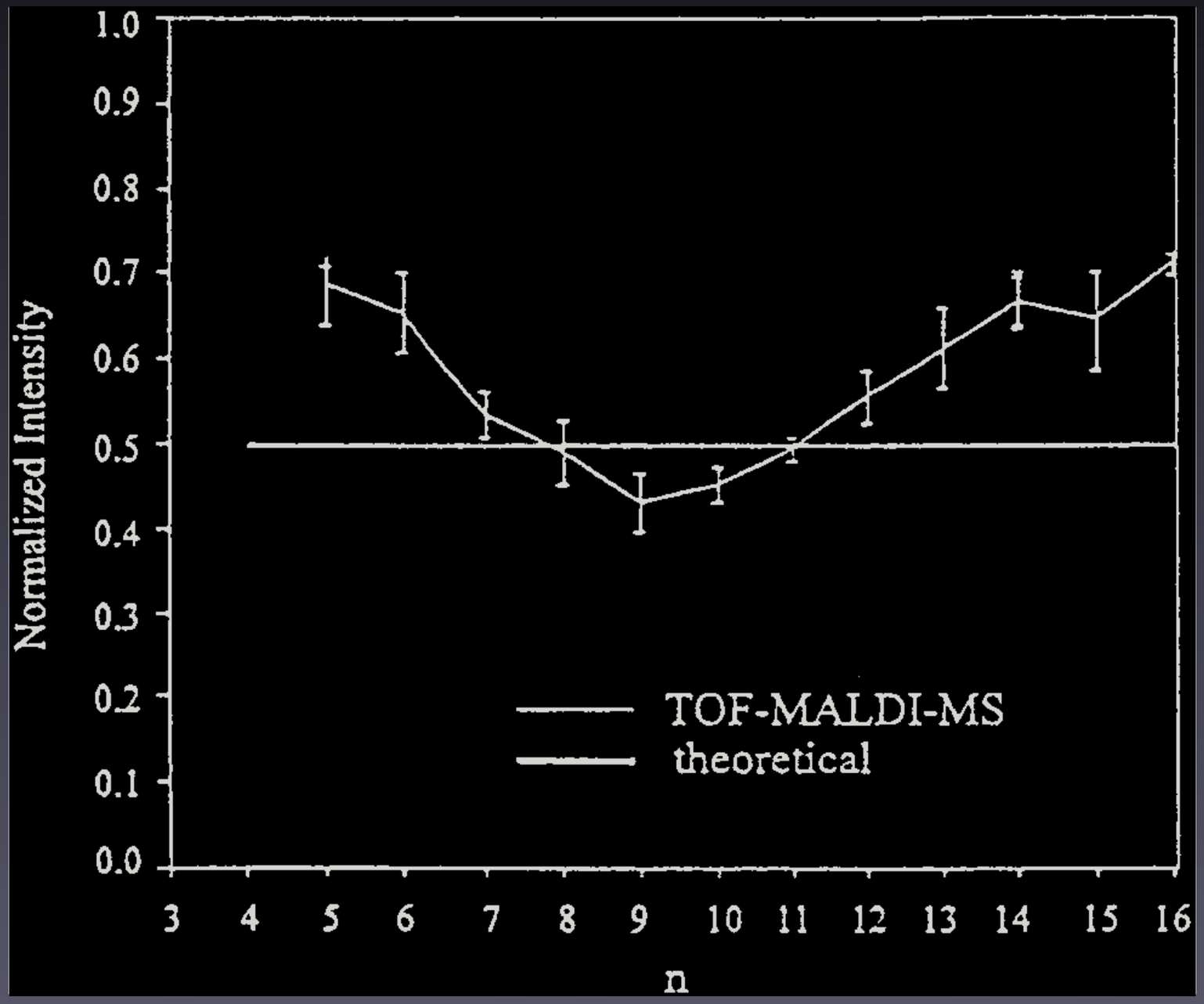
Examples

- Choice of laser power can affect relative abundance depending on chain length
- Figure shows 3 monodisperse PMMA polymers in an equimolar ratio



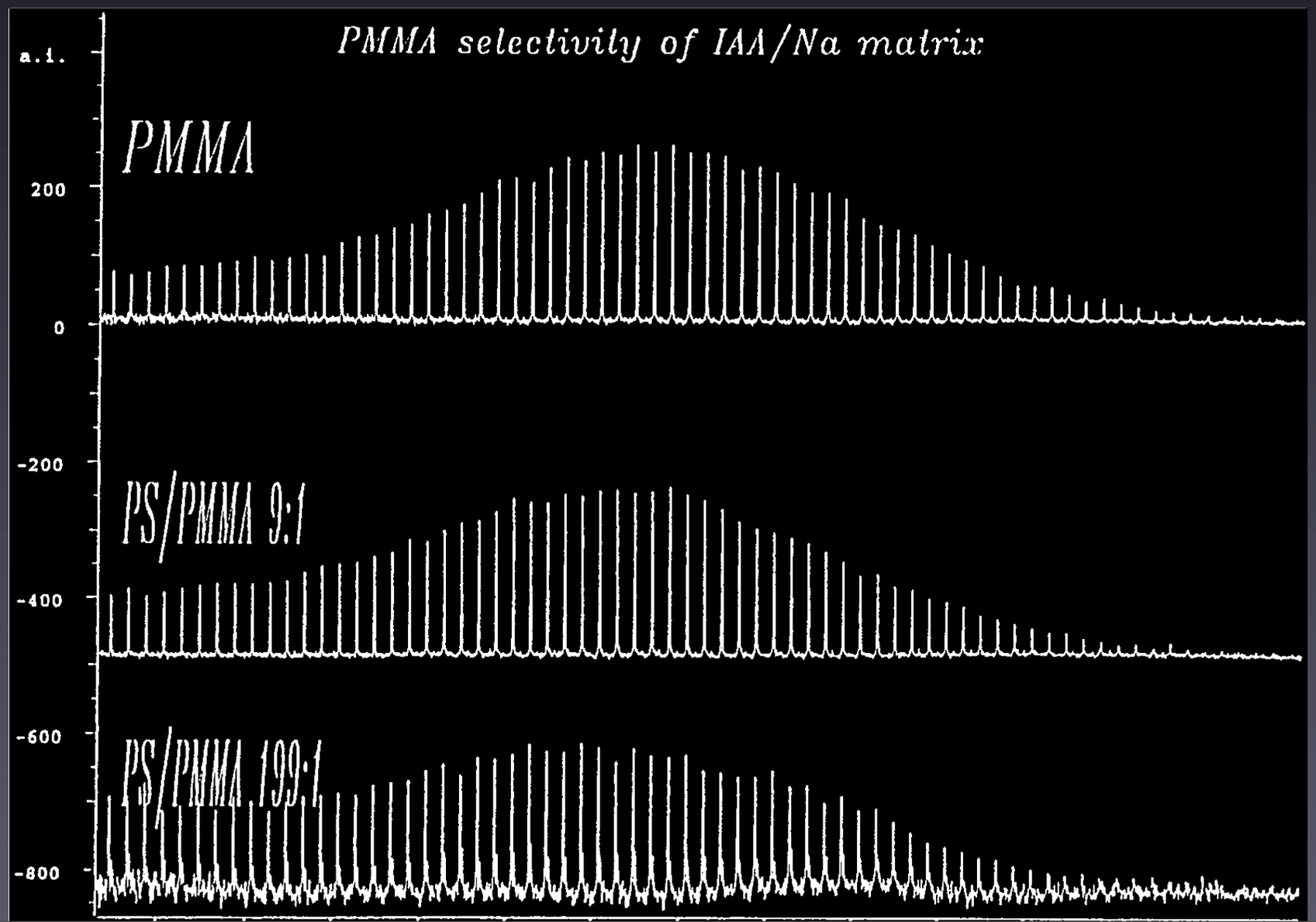
Examples

- Polymers with different end groups can have different ionization efficiencies



Examples: Blends

- Conditions may favor one type of polymer over another
  - analysis of blends can be difficult



Using the data

- Distribution Properties
  - $M_n=\Sigma ma/\Sigma a$
  - $M_w=\Sigma m^2 a/\Sigma ma$
  - $P_d=M_w/M_n$
- Repeat Unit
  - Simply the difference in mass between oligomers
  - Calculate multiple differences and use the mean for best accuracy
  - Monoisotopic masses are most accurate
- End Group
  - Use the remainder of Peak Mass/Repeat Mass
    - Mass could be remainder+n repeat masses
    - Again, use monoisotopic masses if available

Calculation

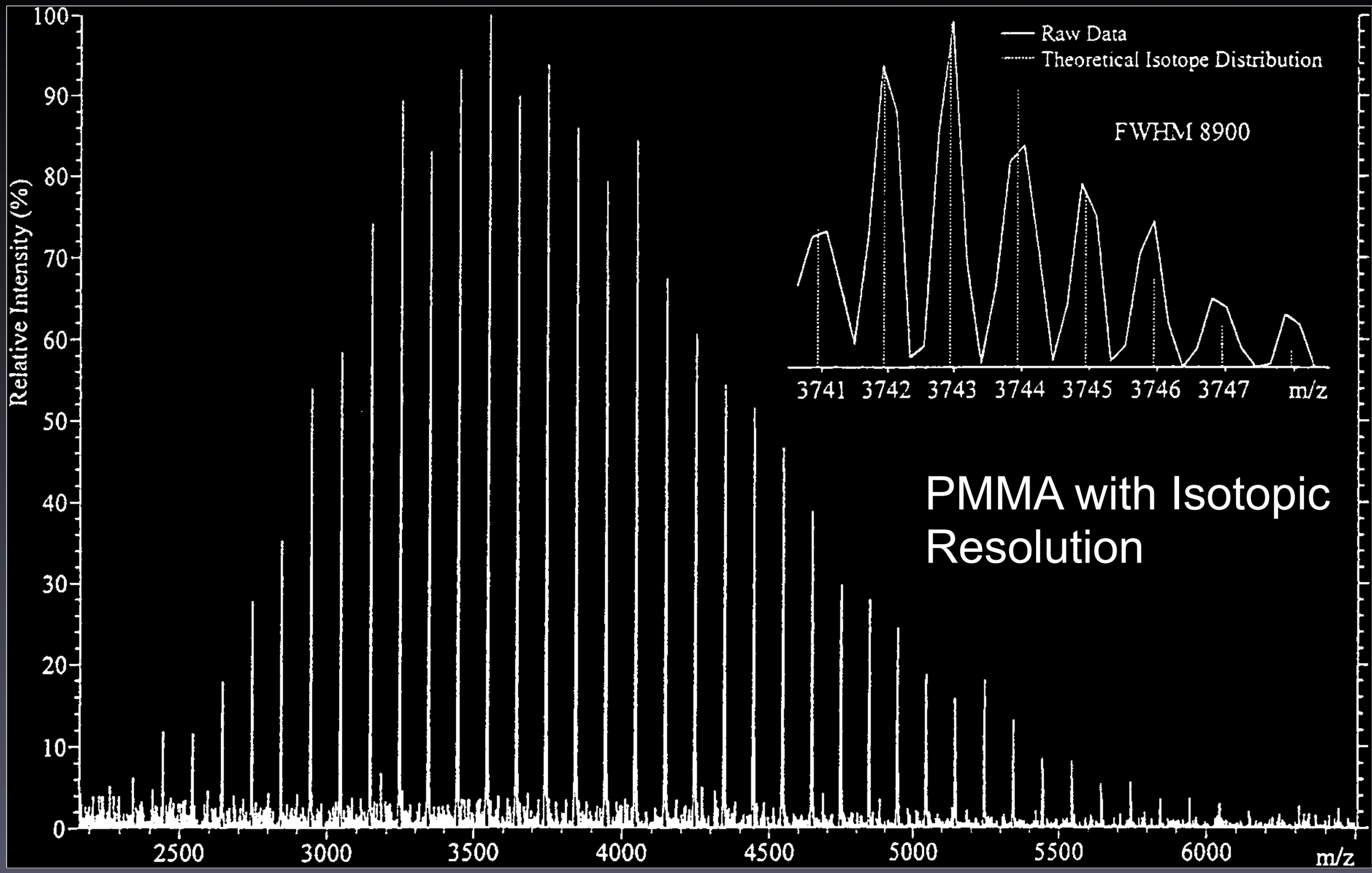
mass	repeat	mass/ repeat	mass% repeat	rem-23
305.3240				
349.3772	44.0532	7	41.0048	18.015
393.4303	44.0531	8	41.0055	18.0157
437.4835	44.0532	9	41.0047	18.0149
481.5366	44.0531	10	41.0056	18.0158
525.5898	44.0532	11	41.0046	18.0148
569.643	44.0532	12	41.0046	18.0148
613.6961	44.0531	13	41.0058	18.016
657.7493	44.0532	14	41.0045	18.0147
701.8024	44.0531	15	41.0059	18.0161

mass	area	mass* area	mass^{2}* area	results
305.3240	125	38166	11652843	
349.3772	175	61141	21361275	M_n
393.4303	250	98358	38696850	515.96
437.4835	350	153119	66987134	M_w
481.5366	575	276884	133329561	533.77
525.5898	665	349517	183702684	P_d
569.643	544	309886	176524272	1.03
613.6961	400	245478	150649161	
657.7493	250	164437	108158535	
701.8024	125	87725	61565826	
sum	3459	1784711	952628143	

Small-Medium Polymers

- MALDI-TOF can give isotopic separation up to ~3-5 kDa
- Repeating unit resolution is possible up to ~50 kDa
- Beyond this only distribution information is possible

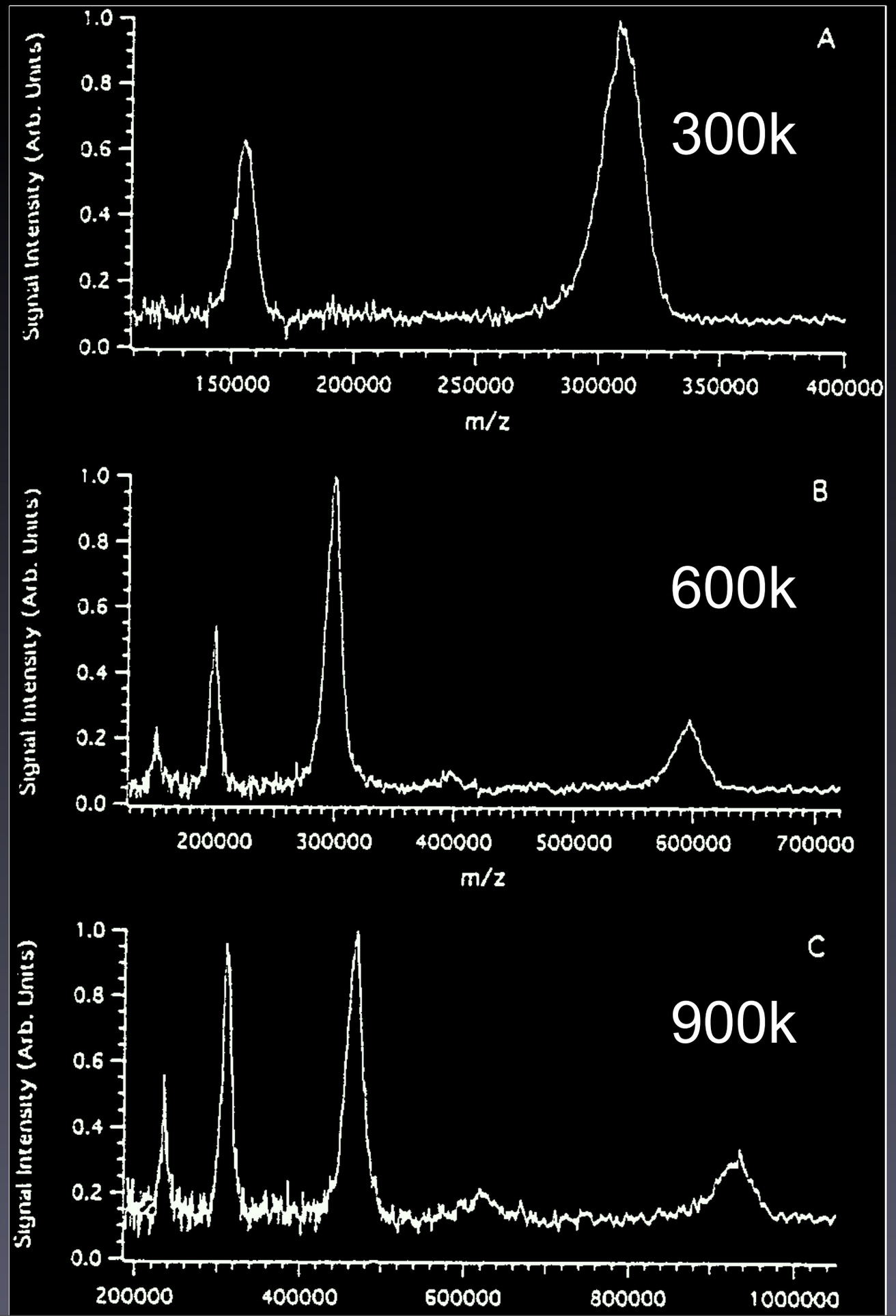
Small-Medium Polymers



PMMA with Isotopic Resolution

Large Polymers

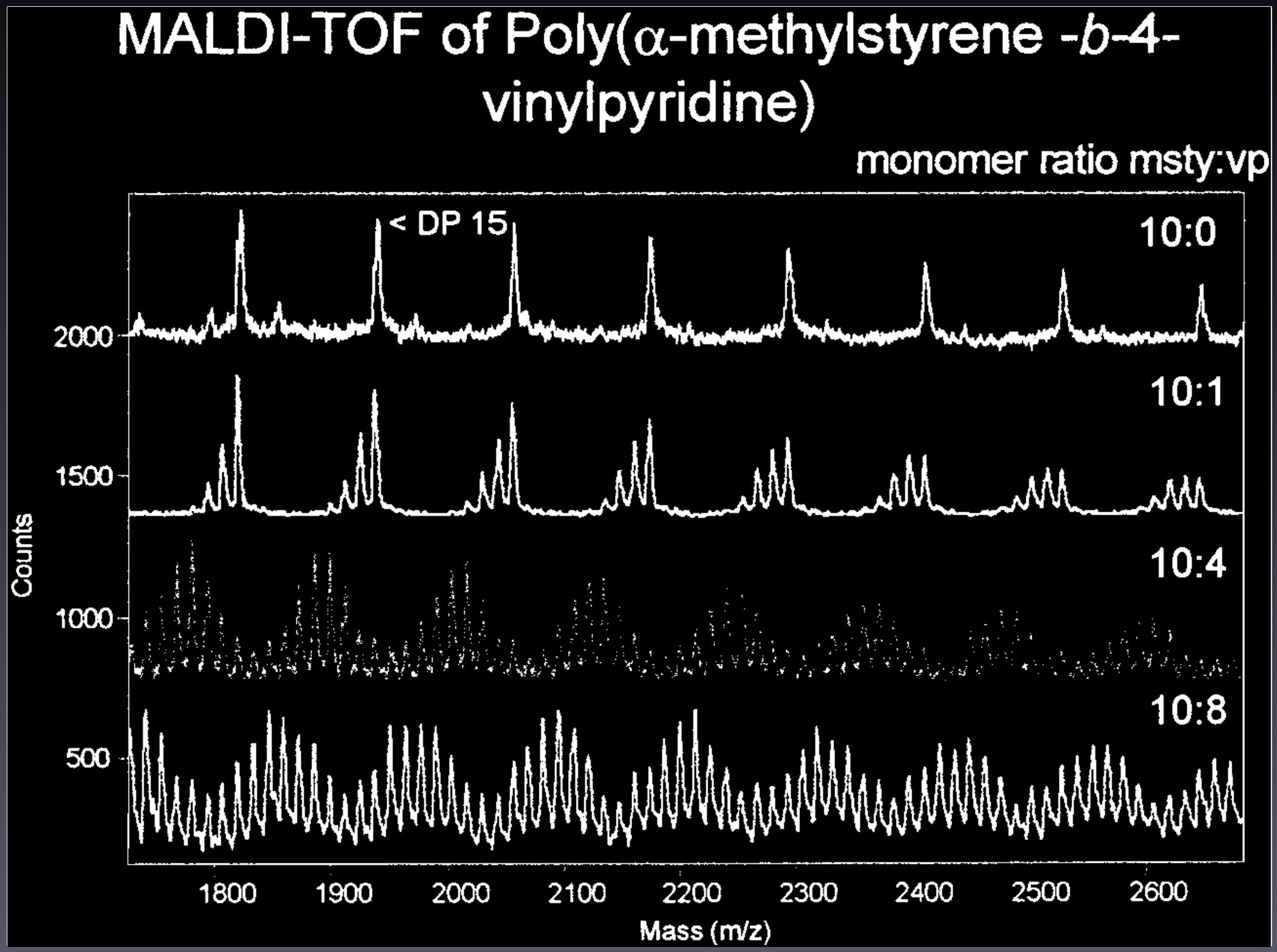
- Even MALDI can give multiple charging
- Repeating-Unit Resolution is not possible
  - Repeating and end group mass cannot be measured



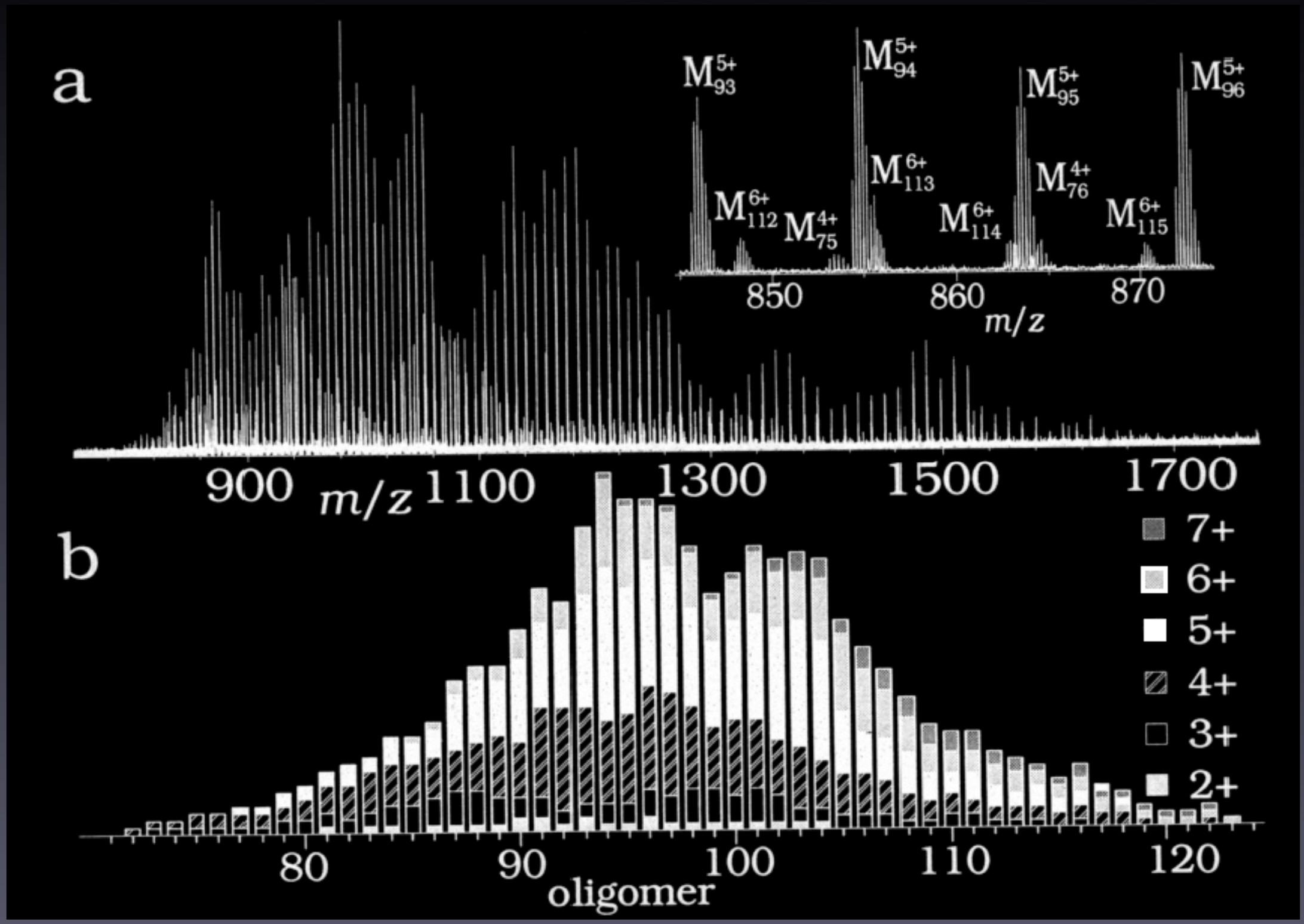
Copolymers

- Copolymer spectra can be complex
  - resolution is important in resolving overlapping distributions
- Determination of chemical composition distribution is possible
- Only composition is determined
  - Differences between random, alternating, block are not detected
- MS/MS can be used to gain such sequence information

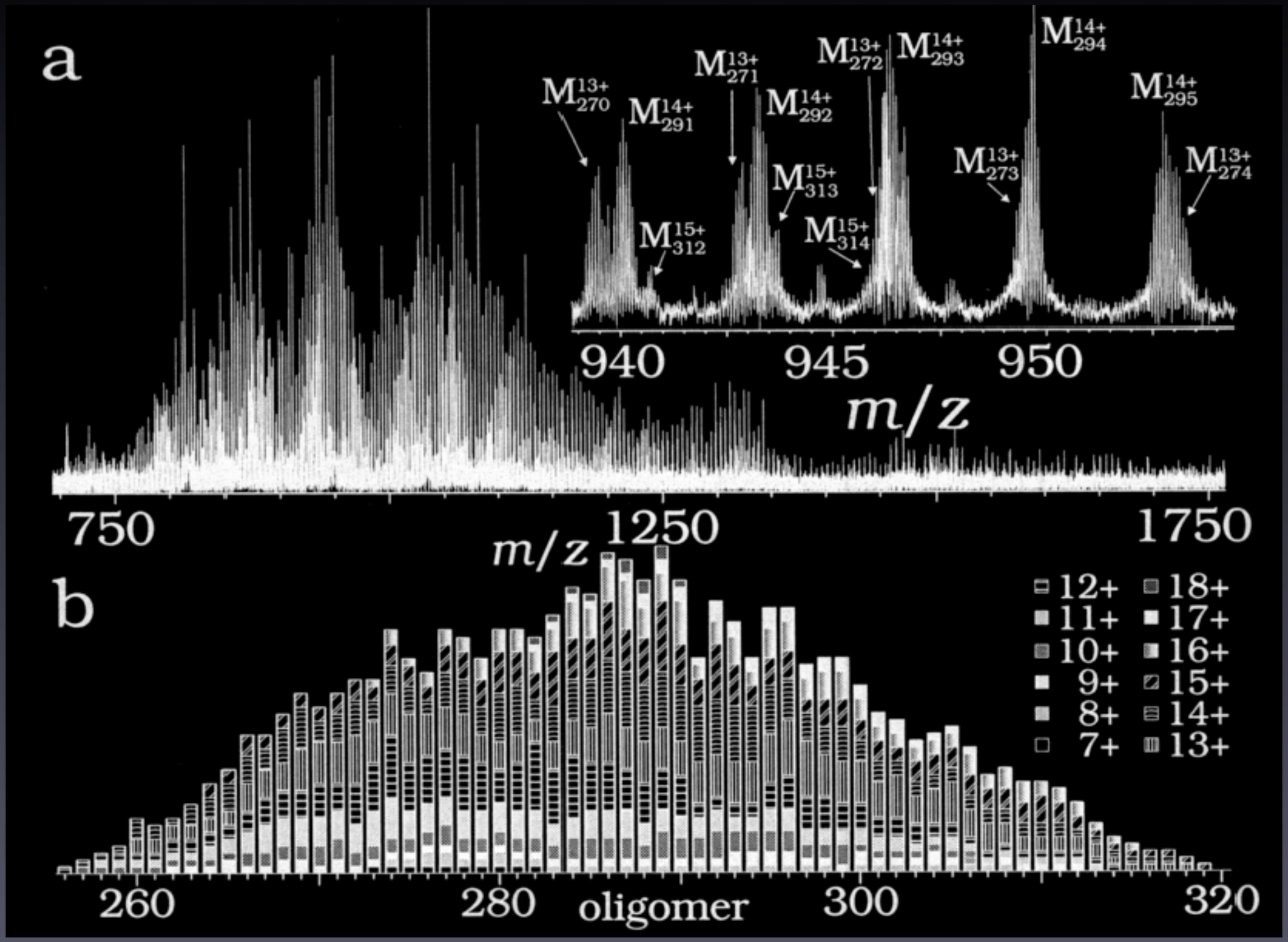
Copolymers


MALDI-TOF of Poly(α-methylstyrene -b-4-vinylpyridine)
monomer ratio msty:vp
< DP 15
10:0
10:1
10:4
10:8
2000
1500
1000
500
Counts
1800
1900
2000
2100
2200
2300
2400
2500
2600
Mass (m/z)

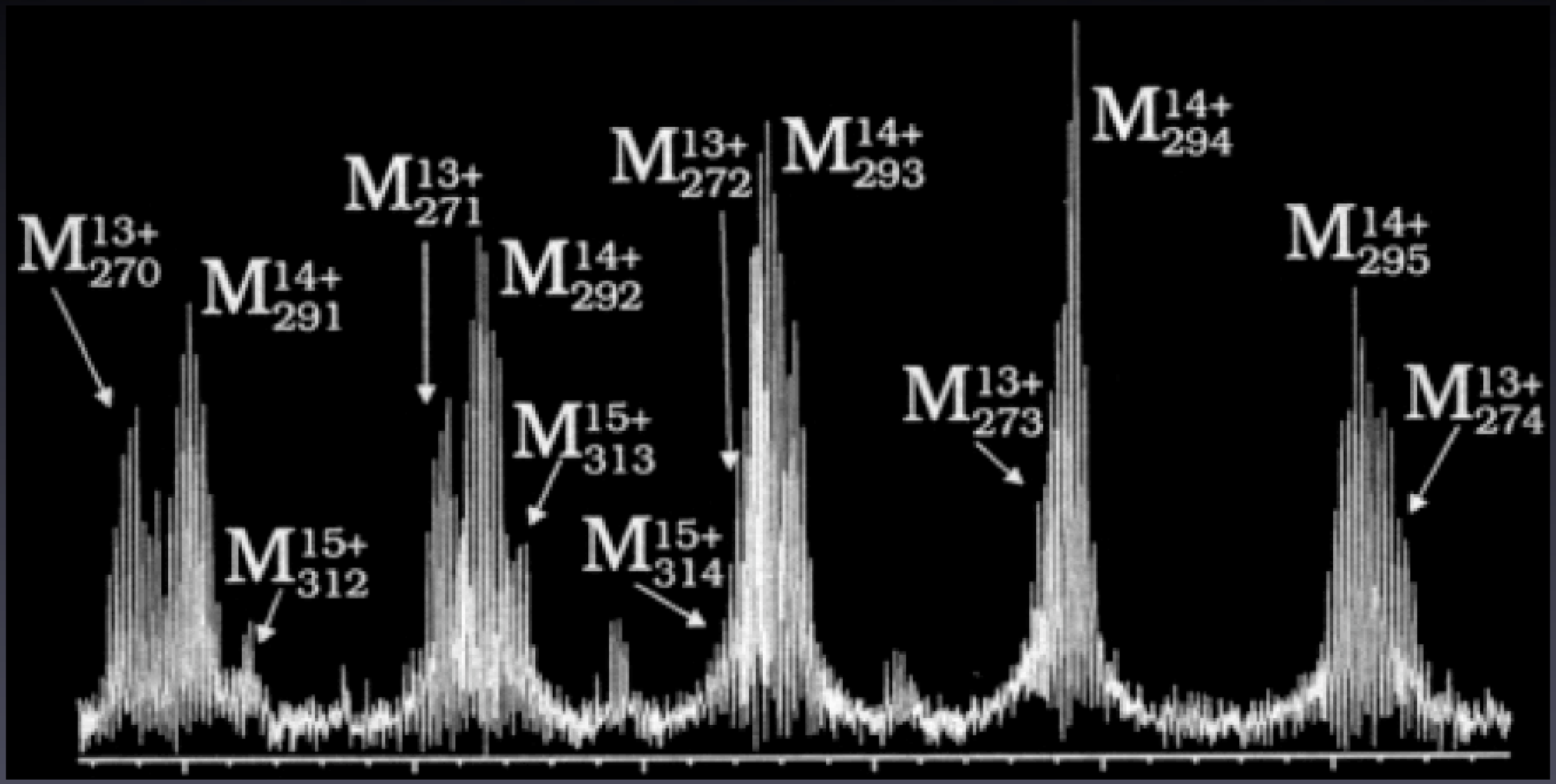
ESI of Polymers: PEG 4000



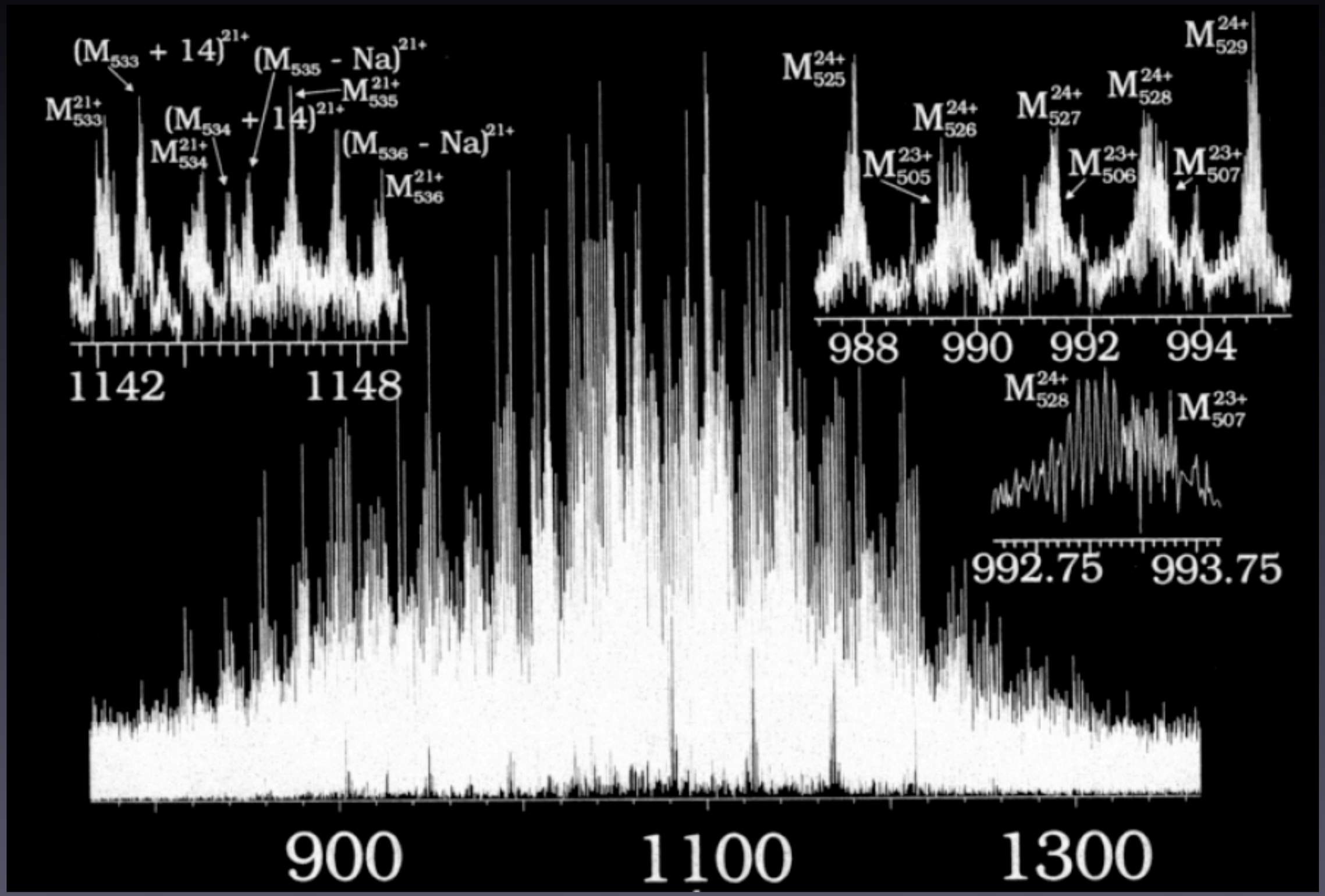
ESI of Polymers 14 kDa



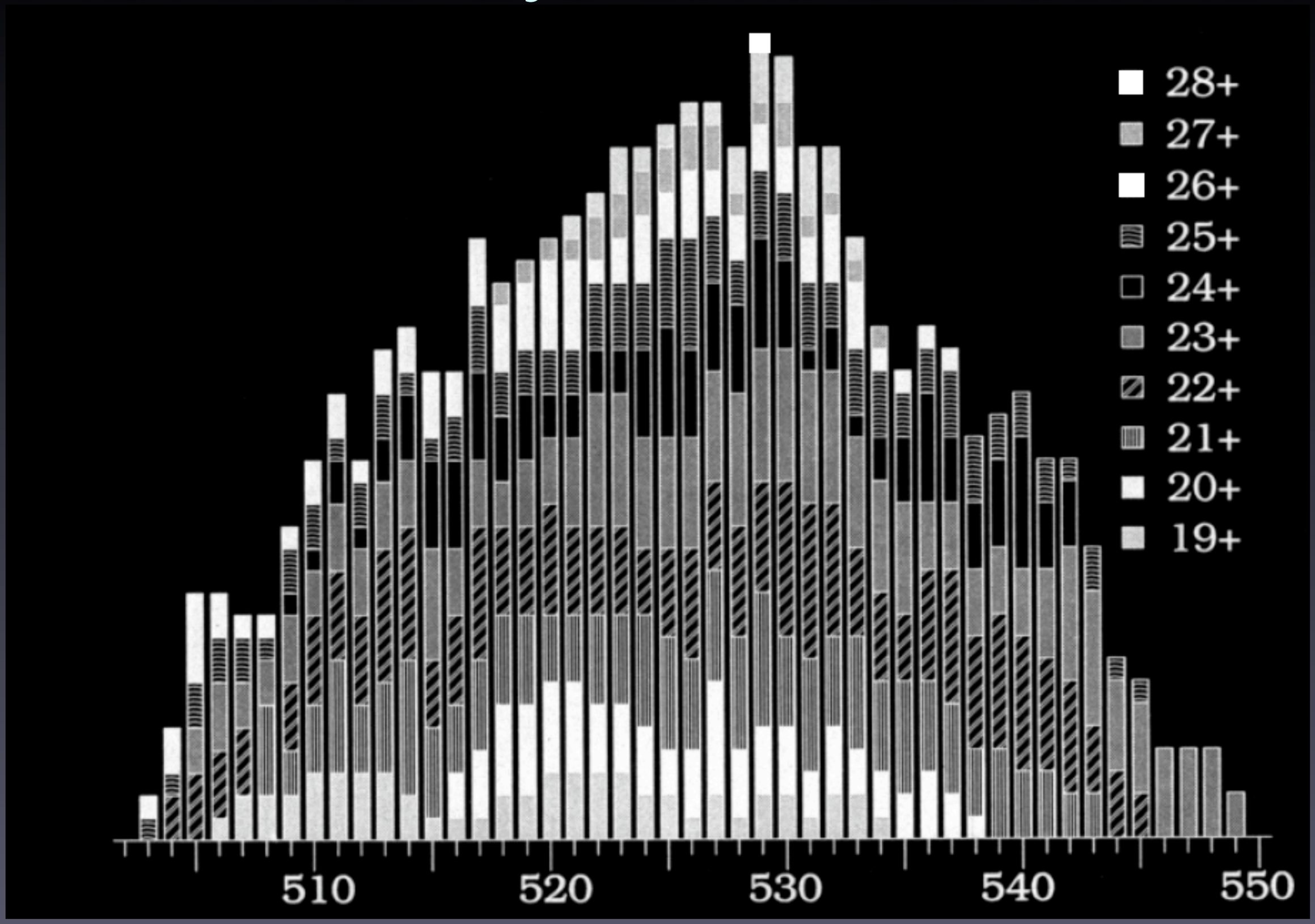
ESI of Polymers: 14kDa



ESI Polymers: 20 kDa



ESI Polymers: 20 kDa



ESI of Polymers

- Complexity of polymer ESI requires very high resolution to resolve overlap of charge states and chain lengths
  - FTMS could be used up to ~50kDa
  - ESI-TOF up to ~10kDa
  - Quadrupole/Ion Trap to ~5 kDa