Polymer Structure by Advanced Mass Spectrometric Methods

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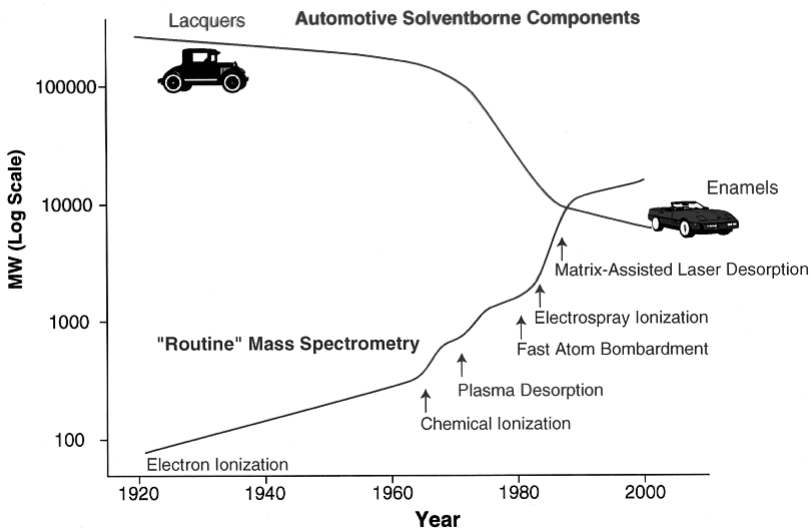
Baltimore, Maryland 12/9-12/10

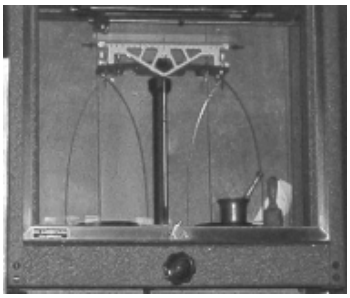
Outline

- Polymers in High-Performance Coatings
- Soft Ionization Methods & Predictability
- Instrumentation
- High Resolution FTMS
- MS/MS Applications
- Coupling to Gel Permeation Chromatography
- Summary/Continuing Studies
- Acknowledgements

Mass Spectrometry of Coatings Components



The **"OLD"** method



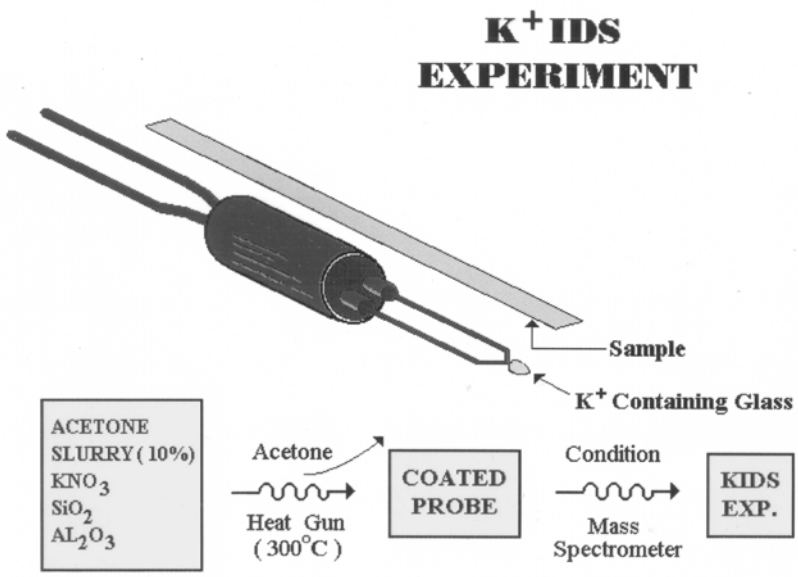
Weighing by the pound

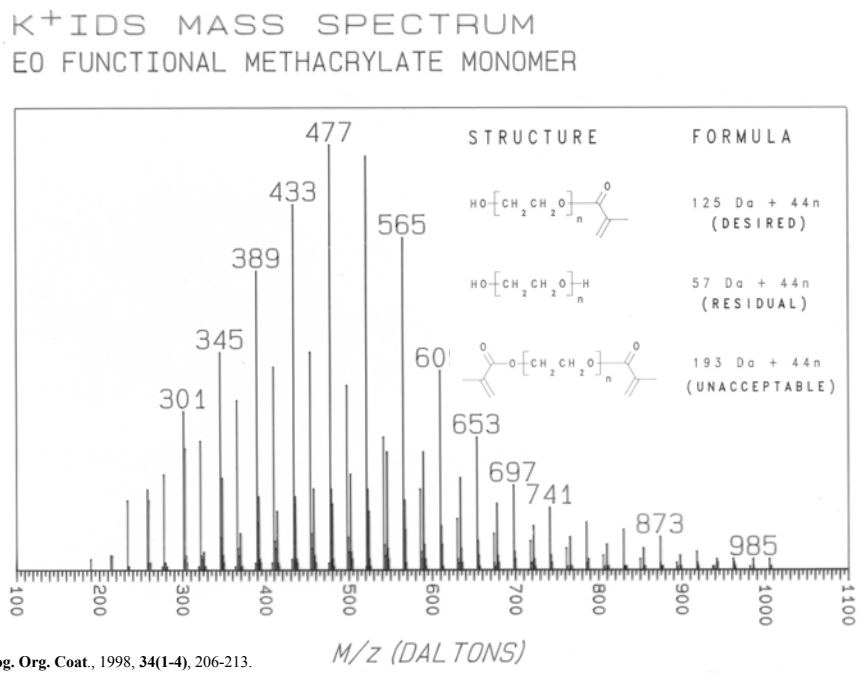
$1000.00/unit

"NEW & IMPROVED"

Weighing molecules in the nanometer size regime

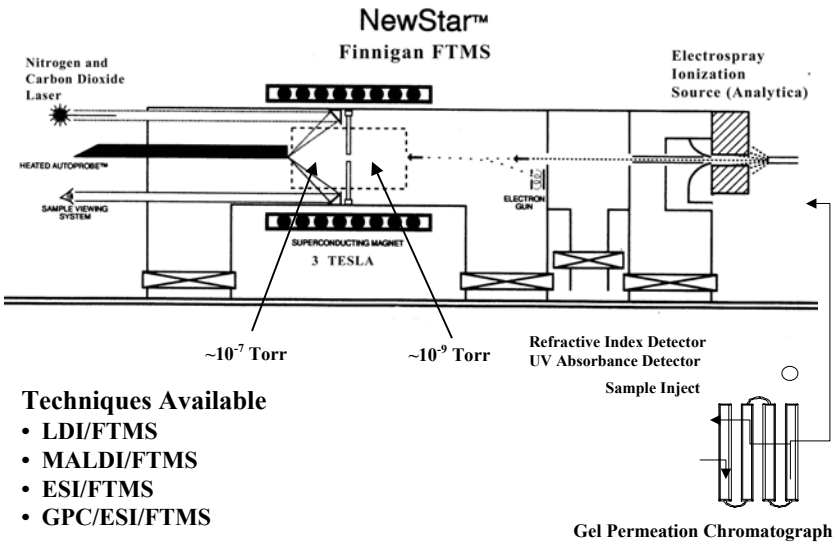
$1,000,000.00/unit





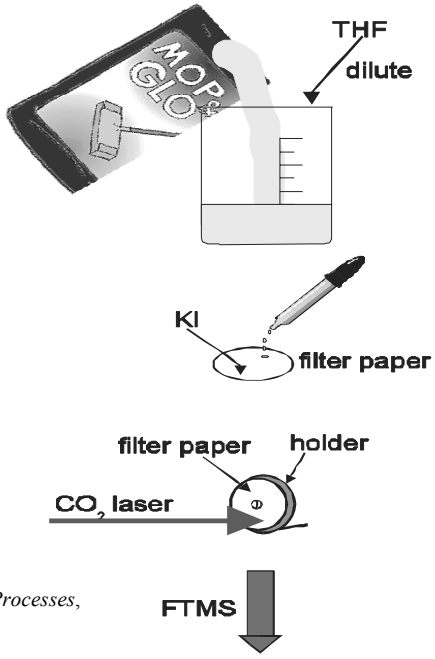
Prog. Org. Coat., 1998, **34(1-4)**, 206-213.

Fourier Transform Mass Spectrometry



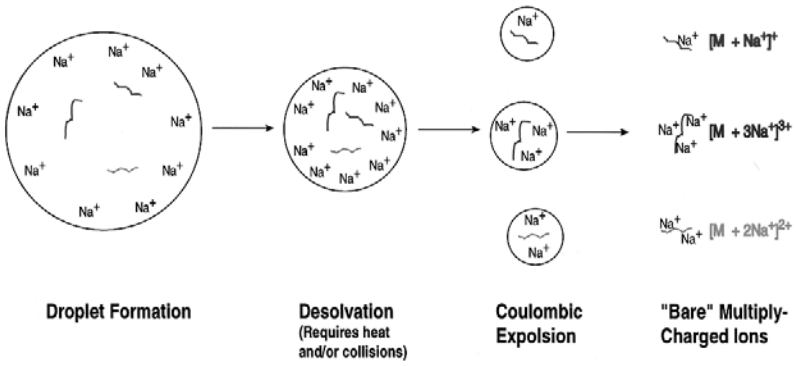
Techniques Available

- **LDI/FTMS**
- **MALDI/FTMS**
- **ESI/FTMS**
- **GPC/ESI/FTMS**



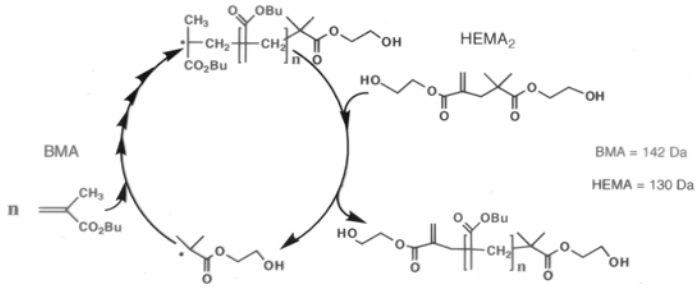
Int. J. Mass Spectrom. Ion Processes, **1996**, 157/158, 379-390.

Ion Formation by Electrospray (Na cation attachment)



Macromonomer Approach to Telechelics

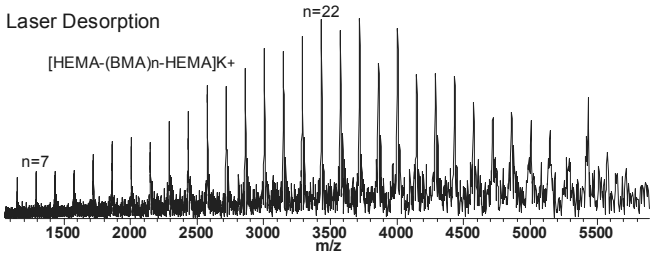
- Statistical Free Radical approach affords too many nonfunctional chains, especially at lower MW
- Synthesize Telechelics using macromonomers ensures functionality of at least 2 for all chains



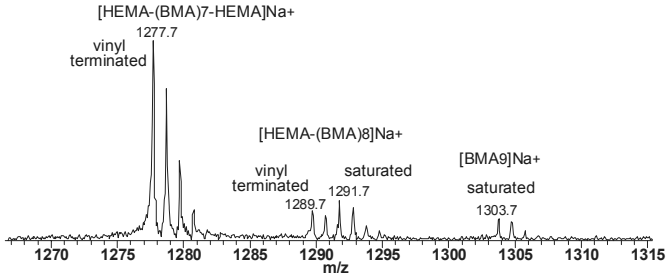
MS -> Monomer Composition of Polymer

HEMA/BMA Copolymer

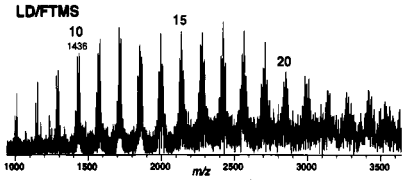
Laser Desorption



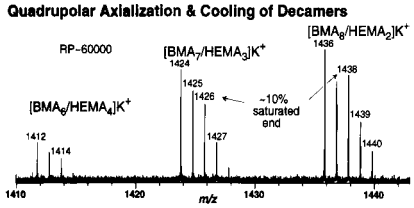
Electrospray Ionization



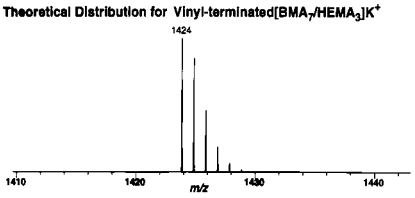
BMA/HEMA COPOLYMER



Quadrupolar Axialization & Cooling of Decamers



Theoretical Distribution for Vinyl-terminated[BMA_7/$HEMA_3$]K^+



Quadrupolar Axialization and Collisional Cooling

(3T Finnigan FT/MS Newstar System w/ Dual Cell)

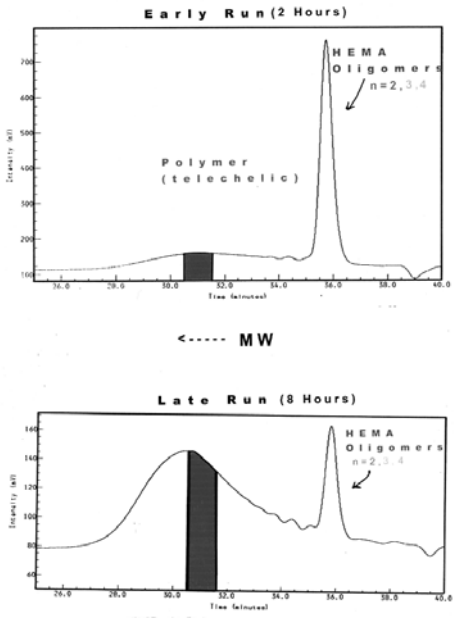
Experimental Conditions

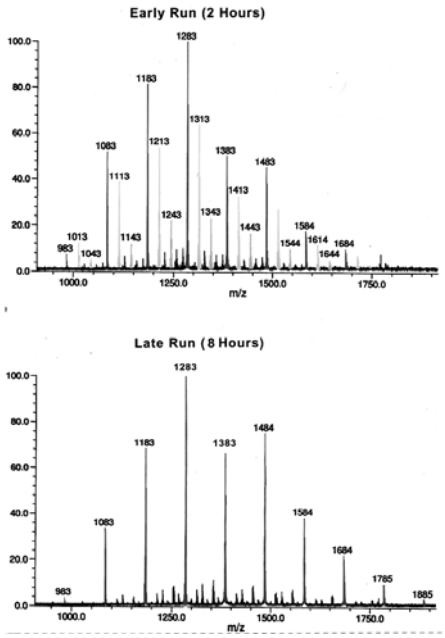
Ions formed by Laser Desorption (with K^+ adduction)
- CO_2 Laser

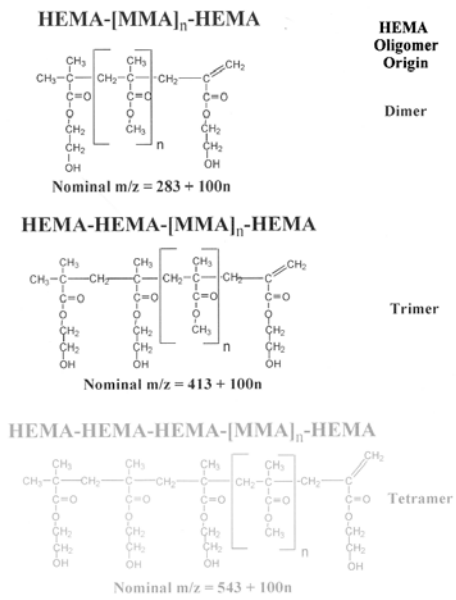
Broadband (200-700 Da) SWIFT Quadrupolar Axialization
- in Source Cell

Cooling with 10^{-6} torr Ar collision gas

Transfer to High Vacuum Analyzer Cell for Chirp Excitation and Heterodyne Detection


Early Run (2 Hours)
HEMA
Oligomers
n=2,3,4
Polymer
(telechelic)
<----- MW
Late Run (8 Hours)
HEMA
Oligomers
n=2,3,4


Early Run (2 Hours)
1283
1183
1313
1083
1213
1383
1483
1113
1413
1243
1343
1443
1584
1013
983
1043
1143
1544
1614
1684
1644
m/z
Late Run (8 Hours)
1283
1484
1183
1383
1584
1083
1684
1785
983
1885
m/z



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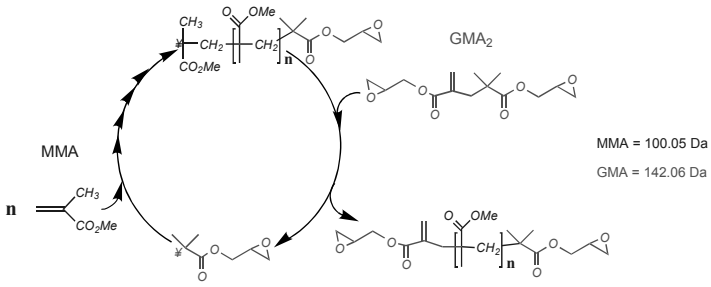
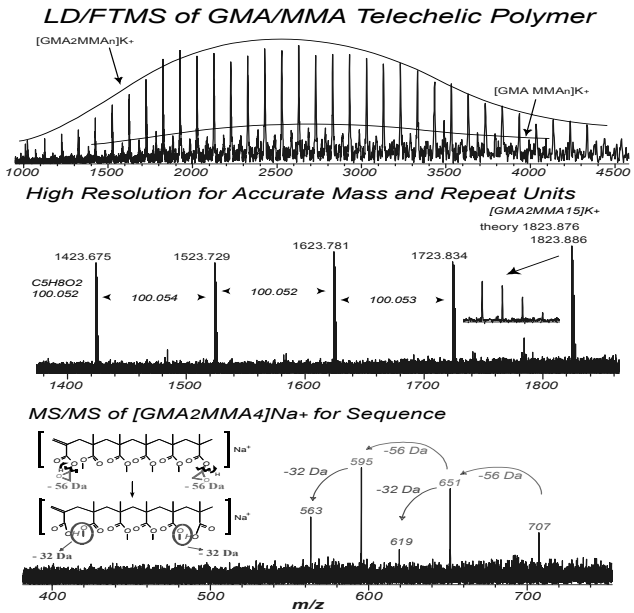
- Telechelics produced via macromonomers ensures functionality of at least two per chain



[GMA-MMAn-GMA]K+ = 38.96 + 284.12 + 100.05n

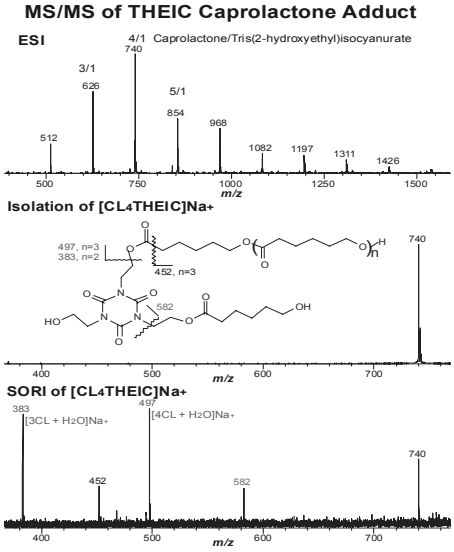
MS -> Monomer Composition of Polymer (Quadrupolar Axialization and Collisional Cooling)

MS/MS -> Sequence Information (SORI)



Proceedings of the 45th ASMS Conference on Mass Spectrometry and Allied Topics, Palm Springs, CA., 1997, p41..

Lamp post versus Star



Long runs of caprolactone
Seen by MS/MS studies

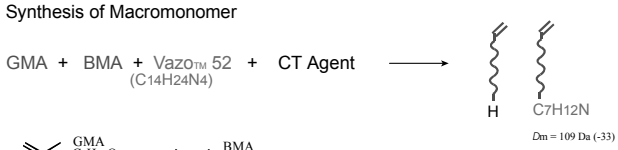
^{13}C shows two types
of hydroxyl groups

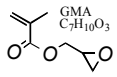
Different physical and Mechanical properties???

Architecturally Designed Graft Polymers

- Macromonomer Technology

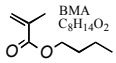
Synthesis of Macromonomer





142.0624 Da

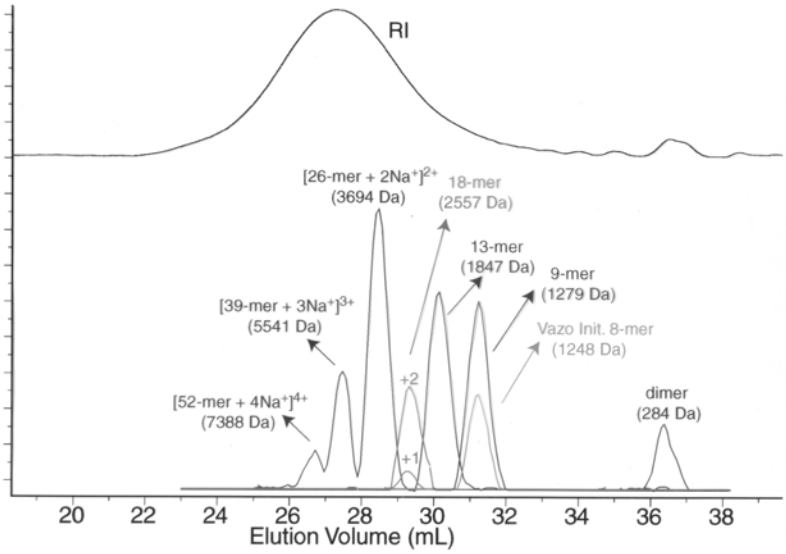
Funtional Monomer (Crosslinks w/ amines and acids)

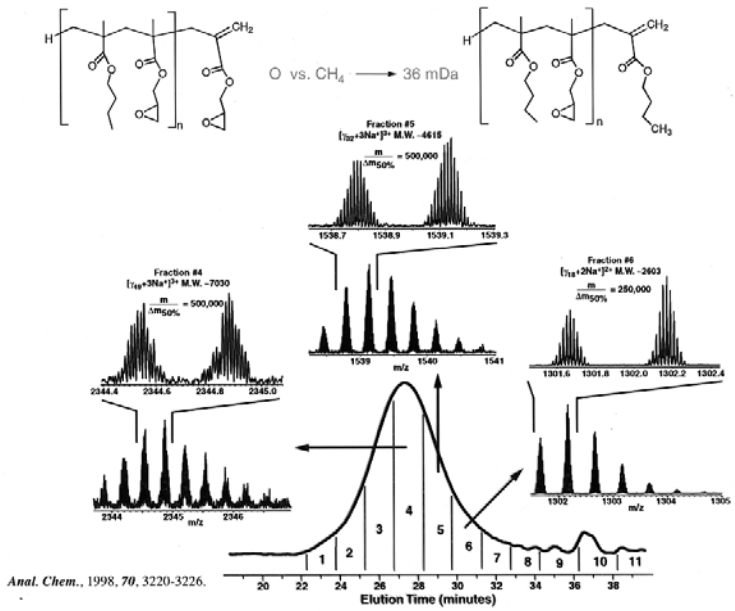


142.0988 Da

Nonfuntional Monomer

Selected Ion Plots of GMA/BMA Oligomers

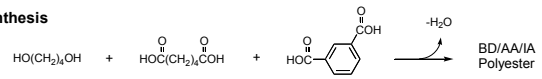




Anal. Chem., 1998, *70*, 3220-3226.

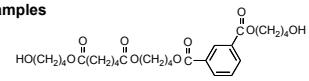
Butanediol / Adipic Acid / Isophthalic Acid Polyester

Synthesis

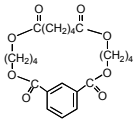


1,4-Butanediol (BD)	Adipic Acid (AA)	Isophthalic Acid (IA)
90 Da	146 Da	166 Da

Examples



Linear OH Capped BD-AA-BD-IA-BD

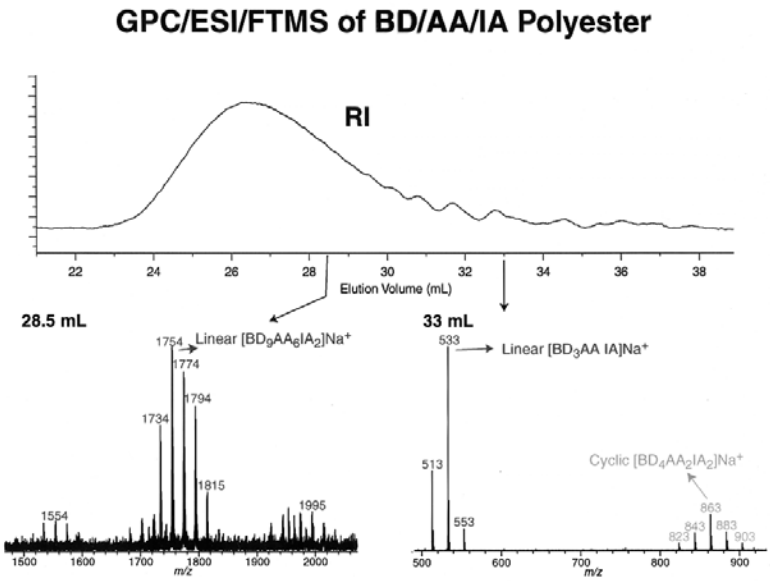


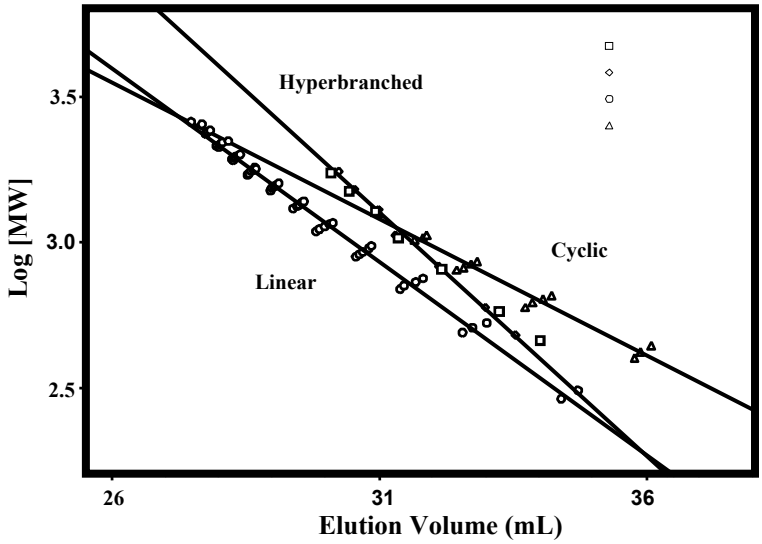
Cyclic BD-AA-BD-IA

Expected $[M]Na^+$

Linear OH Capped 7-mers		Cyclic 6-mers	
BD_4AA_3	713 Da	BD_3AA_3	623 Da
BD_4AA_2IA	733 Da	BD_3AA_2IA	643 Da
$BD_4AA\ IA_2$	753 Da	$BD_3AA\ IA_2$	663 Da
BD_4IA_3	773 Da	BD_3IA_3	683 Da

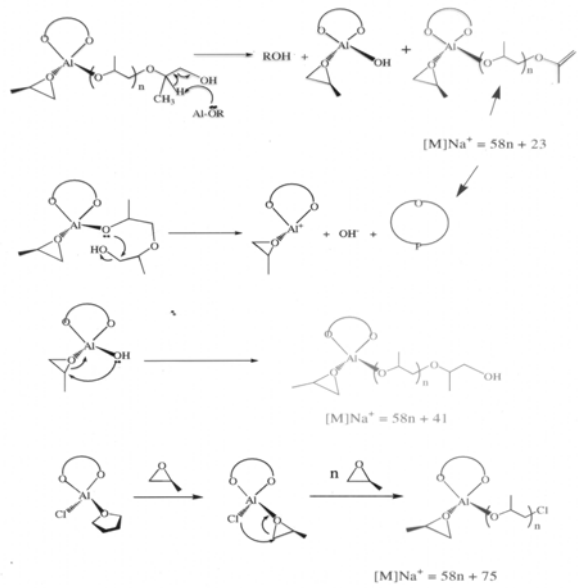
Linear OH/Acid capped oligomers also observed

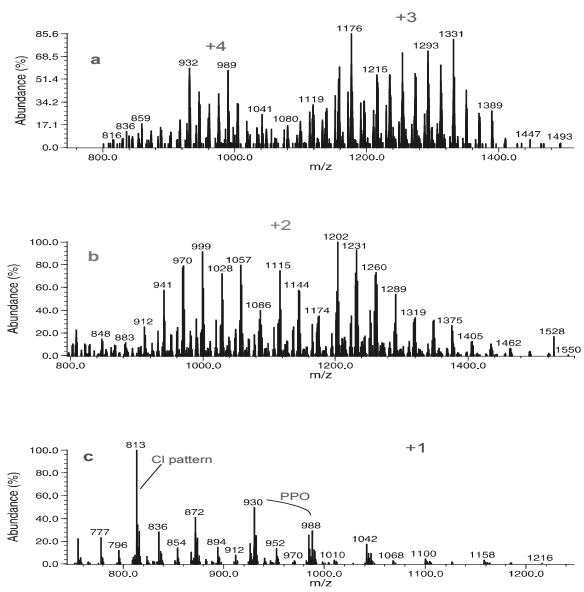


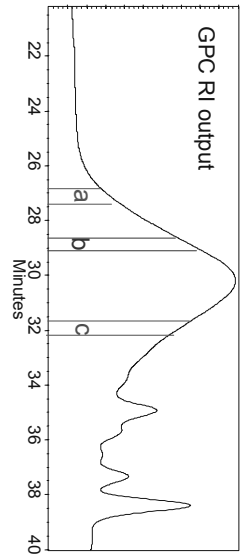


Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.), 2000, **41(1)**, 657-658.

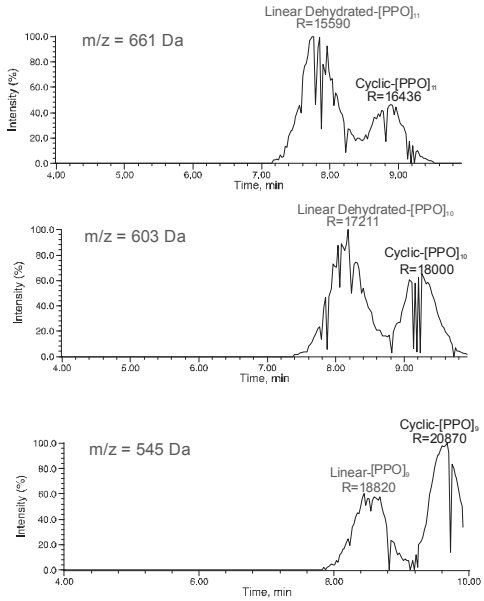
Ring Opening Polymerization







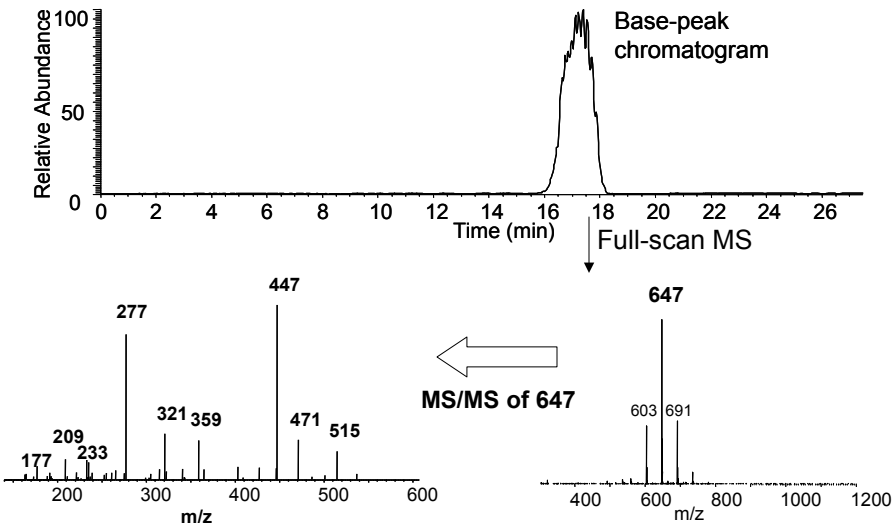
Selected Oligomer Profiles of Isomers separated by GPC/FTMS



Online SEC-API-MS/MS

- C_8H_{17}-C_6H_4-$O(CH_2CH_2O)_nH$
- 2 columns: 30 cm x 7.8 mm i.d. 3-µm PLGel MIXED-E
- APCI: $[M+H]^+$
- Quadrupole ion-trap (LCQ)
- Data-dependent acquisition: full-scan MS followed by MS/MS (product ion)

SEC-APCI-MS/MS of C_8H_{17}-C_6H_4-$O(CH_2CH_2O)_nH$



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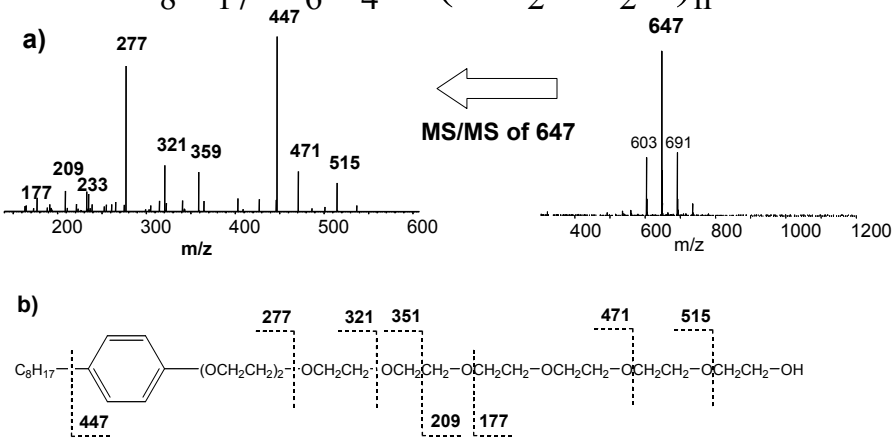

Multiple Detection Size Exclusion Chromatography – ACS Symposium Series – 893, A. M. Striegel, Ed., American Chemical Society: Washington, DC; 2004

Summary/Continuing Studies

Accurate molecular weight data for novel polymer architectures;
- K. Dusek/L. Wilczek (***Polymer,*** 1999)

Capillary GPC, multidimensional separations; Detectors
- L. Prokai/D. Berek (***J. Chromatog. A.,*** 1999)
- M. Liu & P. Maziarz (Intrinsic Viscosity f(MW)

Other cations/mobile phases for electrospray ionization;
- Ag, Cu for hydrocarbon polymers (***ASMS*** 1999)

Multistage MS for sequencing;
- T. Jackson ICI; GTP block vs random (***ASMS*** 1999)
- 2D FTMS for automated MS/MS (***Anal. Chem. 2002***)

Gas phase conformations of oligomers by ion mobility methods;
- Isomeric PPO & BMA/GMA (M. T. Bowers UCSB)

Perform MS/MS experiments across SEC peak using data dependent acquisition for different sizes, architectures, degrees of blockiness.

Acknowledgments

- Dr. David Aaserud (Lubrizol)
- Dr. Wendy Zhong (Wyeth-Ayers)
- Dr. Michael Grady (DuPont)
- Ray Celikay (DuPont)
- Prof. Alan Marshall (FSU/NHMFL)
- Prof. Malcolm Chisholm (OSU)
- Prof. Laszlo Prokai (UF)
- DuPont Marshall R&D Laboratory