Analytica Chimica Acta 932 (2016) 1–21

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Review

Polymer architectures *via* mass spectrometry and hyphenated techniques: A review

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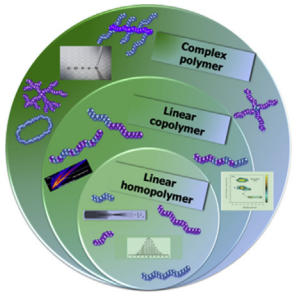
HIGHLIGHTS

- Novel approaches in MS characterization of polymers are discussed.
- Publications on MS and hyphenated strategies toward analysis of polymers architectures are reviewed.
- Computational methods for the interpretation of polymer MS data are encouraged.
- Upcoming expectances using MS-based methods on polymer analysis are suggested.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 July 2015
Received in revised form
7 April 2016
Accepted 16 May 2016
Available online 24 May 2016

Keywords:
Mass spectrometry
Liquid chromatography
Ion mobility
Tandem mass spectrometry
Polymers
Hyphenation

ABSTRACT

This review covers the application of mass spectrometry (MS) and its hyphenated techniques to synthetic polymers of varying architectural complexities. The synthetic polymers are discussed as according to their architectural complexity from linear homopolymers and copolymers to stars, dendrimers, cyclic copolymers and other polymers. MS and tandem MS (MS/MS) has been extensively used for the analysis of synthetic polymers. However, the increase in structural or architectural complexity can result in analytical challenges that MS or MS/MS cannot overcome alone. Hyphenation to MS with different chromatographic techniques (2D × LC, SEC, HPLC etc.), utilization of other ionization methods (APCI, DESI etc.) and various mass analyzers (FT-ICR, quadrupole, time-of-flight, ion trap etc.) are applied to overcome these challenges and achieve more detailed structural characterizations of complex polymeric systems. In addition, computational methods (software: MassChrom2D, COCONUT, 2D maps etc.) have also reached polymer science to facilitate and accelerate data interpretation. Developments in technology and the comprehension of different polymer classes with diverse architectures have significantly improved, which allow for smart polymer designs to be examined and advanced. We present specific examples covering diverse analytical aspects as well as forthcoming prospects in polymer science.

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http://dx.doi.org/10.1016/j.aca.2016.05.024
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Abbreviations

AUC	Analytical ultracentrifuge
AF4	Asymmetric flow field-flow fractionation
APCI	Atmospheric pressure chemical ionization
AROP	Anionic ring opening polymerization
ASAP	Atmospheric solid analysis probe
ATRP	Atom transfer radical polymerization
CCS	Collisional cross section
CE	Capillary electrophoresis
CI	Chemical ionization
CAD	Collision activated dissociation
CZE	Capillary zone electrophoresis
Đ	Dispersity
DESI	Desorption electrospray ionization
DMSS	Dimethylsilylstyrene
ECD	Electron capture dissociation
EI	Electron ionization
ELSD	Evaporative light scattering detector
EO	Ethylene oxide
ESI	Electrospray ionization
ETD	Electron transfer dissociation
FFF	Field-flow fractionation
FT-ICR	Fourier transform-ion cyclotron resonance
GC	Gas chromatography
HPLC	High-performance liquid chromatography
ICR	Ion cyclotron resonance
IM-MS	Ion mobility-mass spectrometry
IR	Infrared
ISD	In-source decay
LAC	Liquid adsorption chromatography
LACCC	Liquid adsorption chromatography at critical conditions
LC	Liquid chromatography
LDI	Laser desorption ionization
LS	Light scattering
MALDI	Matrix-assisted laser desorption/ionization
MD	Molecular dynamics
MS	Mass spectrometry
MS/MS	Tandem mass spectrometry
NMP	Nitroxide-mediated radical polymerization
NMR	Nuclear magnetic resonance
NP	Normal phase
PAA	Poly(acrylic acid)
PAMAM	Poly(amidoamine)
PB	Poly(butadiene)
PBS	Poly(butadiene succinate)
PBT	Poly(butylene terephthalate)
PCL	Poly(caprolactone)
PDMS	Poly(dimethylsiloxane)
PE	Poly(ethylene)
PEEK	Poly(ether ether ketone)
PEI	Poly(ethylenimine)
PEO	Poly(ethylene oxide)
PET	Poly(ethylene terephthalate)
PHEMA	Poly(hydroxyethylmethacrylate)
PI	Poly(*iso*prene)
PIB	Poly(*iso*butylene)
PLA	Poly(lactide)
PLGA	Poly(lactic-*co*-glycolic acid)
PLUMS	Polymer labeling using mass spectrometry
PMA	Poly(methyl acrylate)
PMAA	Poly(methacrylic acid)
PMMA	Poly(methyl methacrylate)
P*n*BA	Poly(*n*-butyl acrylate)
PO	Propylene oxide
POM	Poly(oxymethylene)
PP	Polypropylene
PPG	Poly(propylene glycol)
PPI	Poly(propylene imine)
PPO	Poly(propylene oxide)
PS	Polystyrene
PSD	Post-source decomposition
PSS	Poly(styrene sulphonate)
P*t*BA	Poly(*t*-butyl acrylate)
P*t*BMA	Poly(*t*-butyl methacrylate)
PVAc	Poly(vinyl acetate)
PVAl	Poly(vinyl alcohol)
PVP	poly(*N*-vinyl pyrrolidone)
Py/GC	pyrolysis/gas chromatography
Q	Quadrupole
RAFT	Reversible addition-fragmentation chain transfer
RI	Refractive index
RP	Reversed phase
RP-TGIC	Reverse phase-temperature gradient interaction chromatography
SAXS	Small angle X-ray scattering
SEC	Size exclusion chromatography
SG1	*N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethyl propyl)
SID	Surface-induced dissociation
SIMS	Secondary ionization mass spectrometry
SORI	Sustained off resonance irradiation
SL	Surface layer
SPME/GC	Solid phase microextraction/gas chromatography
TA-APGD	Thermal-assisted atmospheric pressure glow discharge
ThFFF	Thermal field-flow fractionation
TMPO	Trimethylolpropaneoxetane
ToF	Time-of-flight
UV	Ultraviolet

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