Applications note

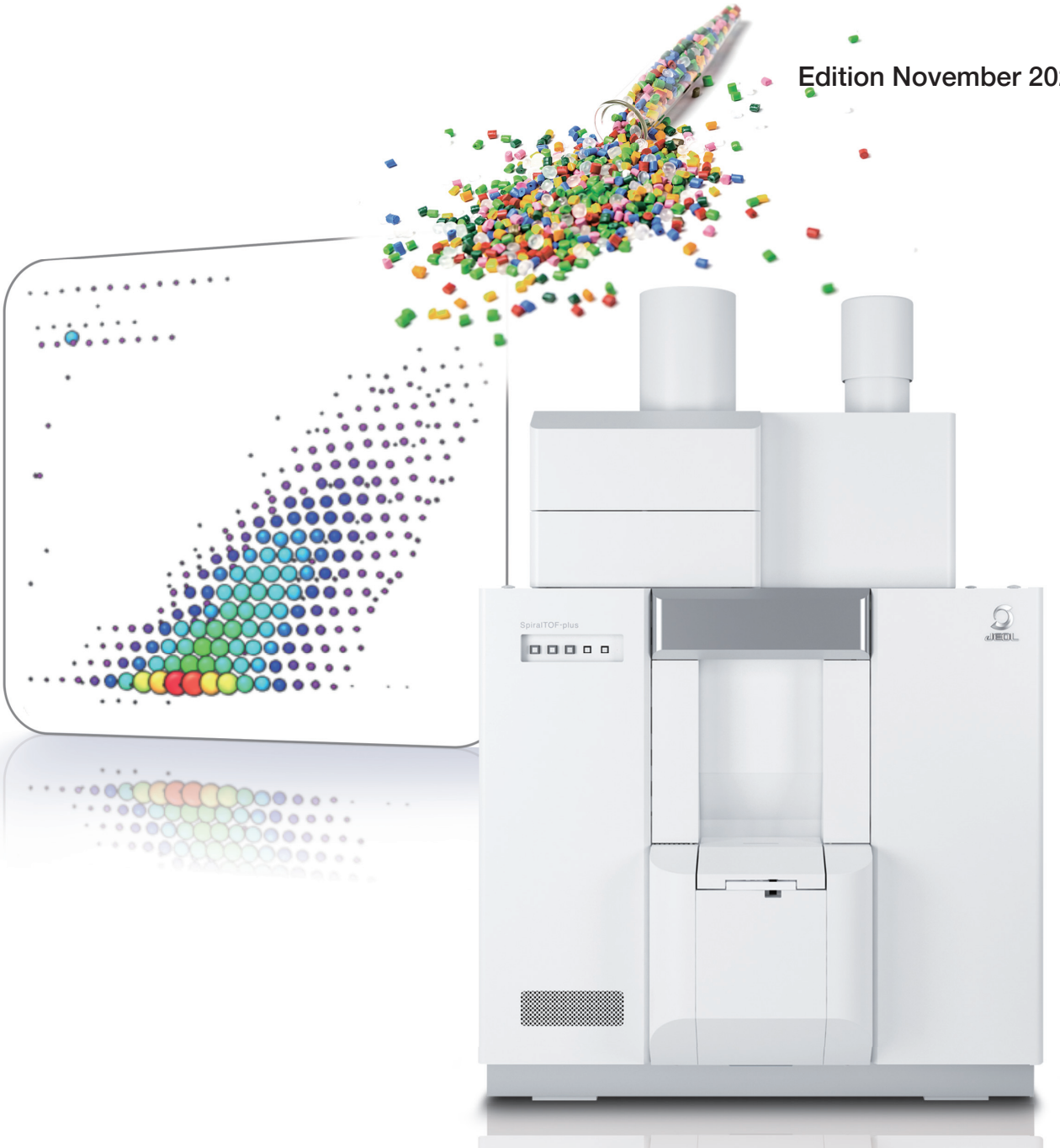
Ultra-High Mass-Resolution
MALDI-TOFMS System

Solutions for Innovation

JMS-S3000 SpiralTOF™ series

Polymer Mass Spectra Collection

Edition November 2021



JEOL Ltd.

Table of Contents

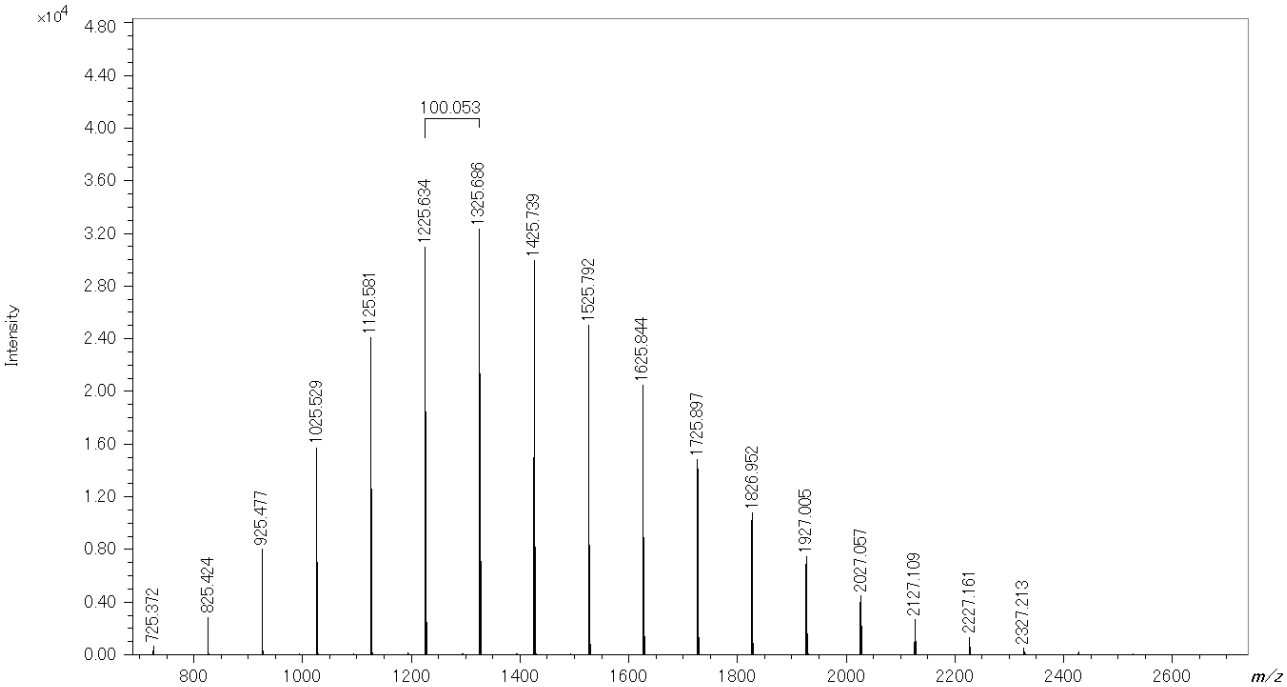
Abbreviations

Abbreviation	Description
DCTB	*trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene] malononitrile
CHCA	α-cyano-4-hydroxy cinnamic acid
DHB	2,5-Dihydroxybenzoic Acid
HABA	2-(4-Hydroxyphenylazo)benzoic acid
THAP	2′,4′,6′-Trihydroxyacetophenone monohydrate
NaTFA	Sodium trifluoroacetate
AgTFA	Silver trifluoroacetate

This booklet is a collection of polymer mass spectra acquired by using JMS-S3000 SpiralTOF™-plus matrix-assisted laser desorption/ionization time-of-flight mass spectrometers (MALDI-TOFMS).
Please refer the legend on page iii regarding the information attached to each mass spectrum.
Note that none of the mass spectra in this booklet shows a guaranteed performance specification of the mass spectrometer.

Legend

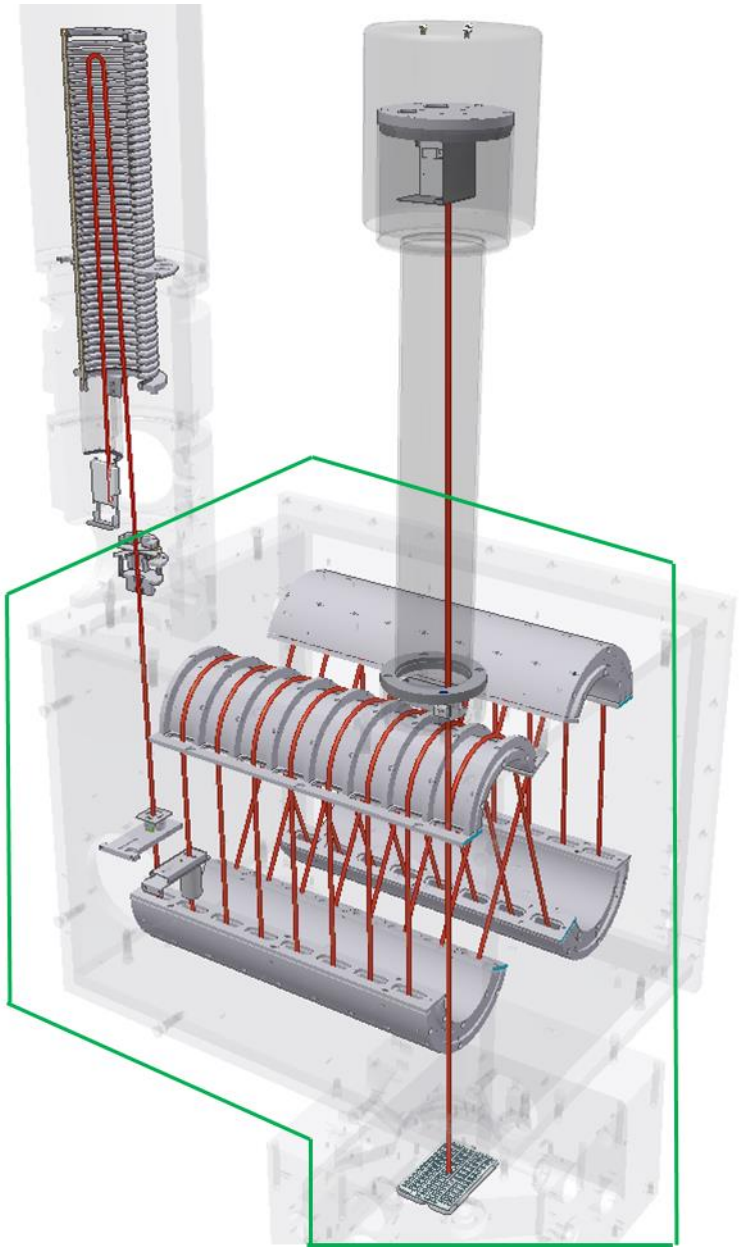
PMMA (poly(methyl methacrylate))



Structure	$H[CH_2C(CH_3)(CO_2CH_3)]_nH$; $H(C_5H_8O)_nH$	Two formulae, one showing structural information and the other showing elemental composition(s) of the repeating unit(s). If the end groups are unknown, the formula is shown as, for example: $-(C_5H_8O)_n-$
Ion Species	$[M+Na]^+$	Detected ion species
Molecular weight Information	M_n 1498; M_w 1559; D 1.041	Molar mass information calculated from the observed mass spectrum, NOT the values declared by the manufacturer.
Matrix	DCTB	Matrix used for the measurement
Cationization agent	NaTFA	Cationization agent used for the measurement
Mode	SpiralTOF:Positive ion	Mass analyzer mode and polarity of ions detected.

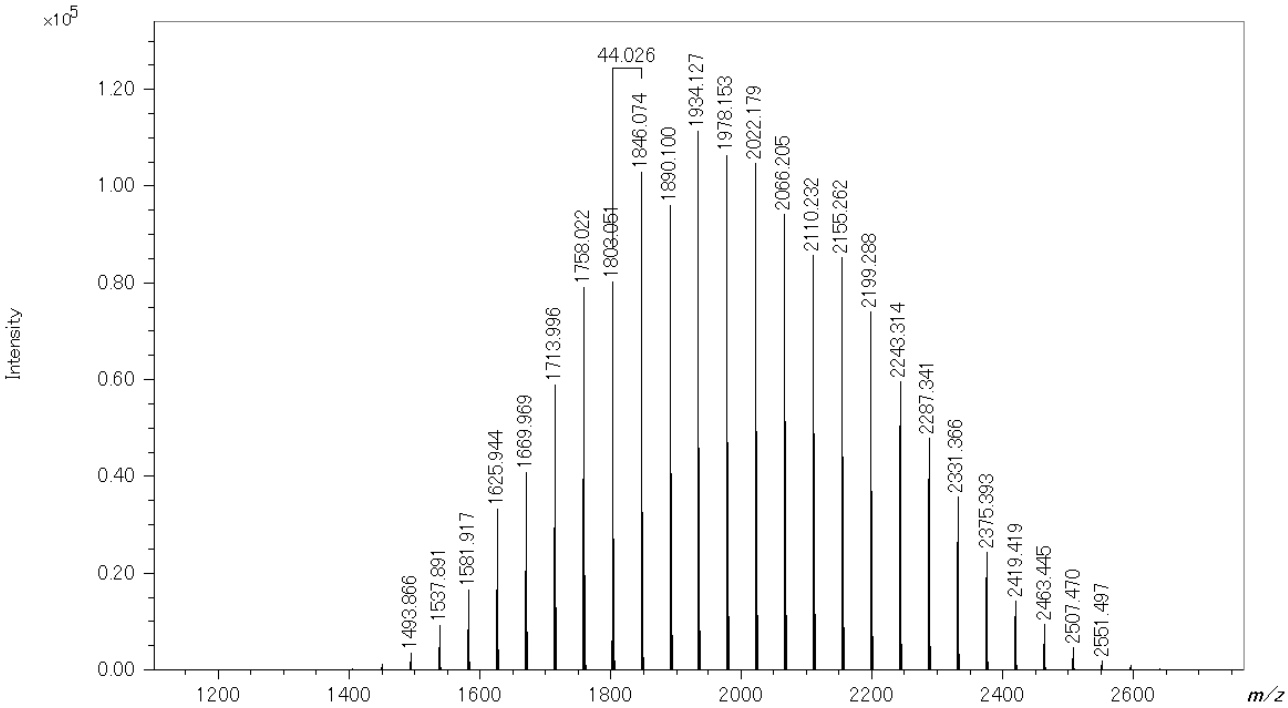
KMD (Kendrick Mass Defect) plots generated by the msRepeatFinder software are shown for the polymers other than homopolymers with only one kind of end groups.
RKM (Remainder of Kendrick Mass) plots generated by the msRepeatFinder software and estimated product ion structures are shown for TOF-TOF (tandem MS) product ion mass spectra.

SpiralTOF Mode



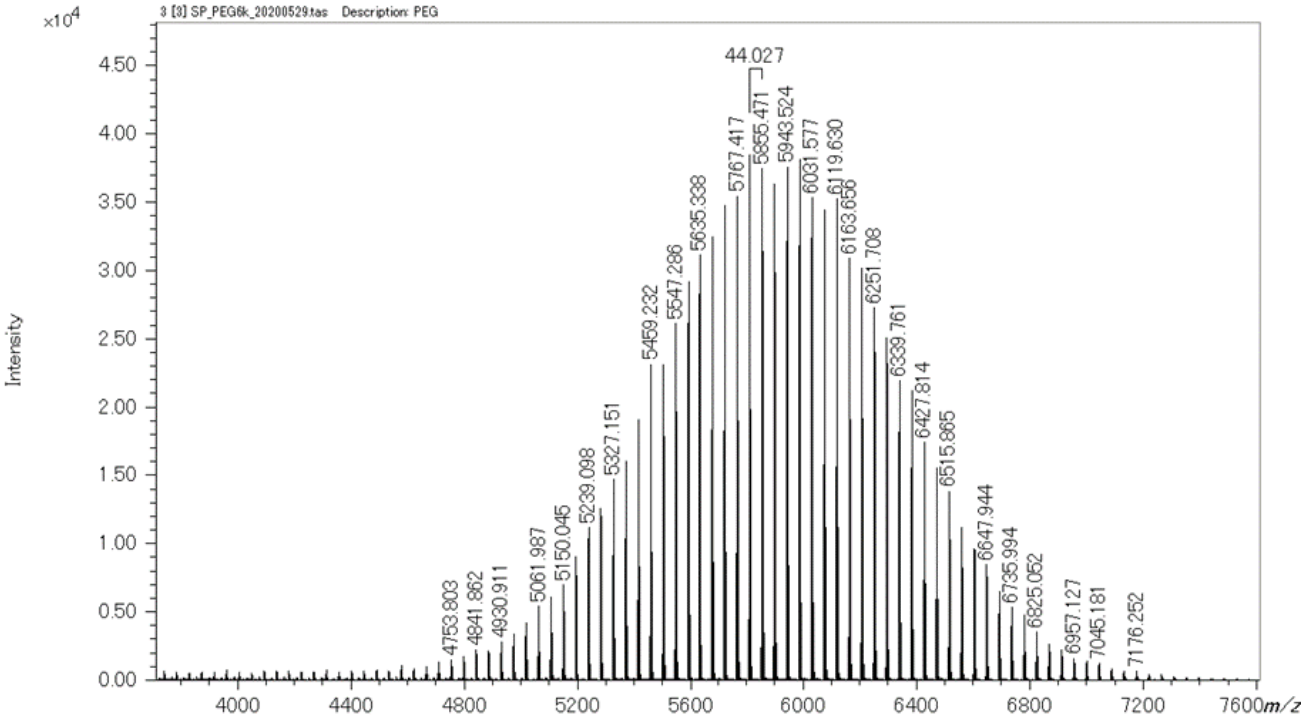
- Ultra-high mass-resolution achieved with JEOL's patented Spiral Ion Trajectory TOFMS.
- High mass-resolution and high mass-accuracy over a wide mass range – essential for polymer analysis.
- Chemical noise is reduced by eliminating post source decay (PSD) ions with electrostatic sectors – minor components can be clearly detected.

PEO (poly(ethylene oxide)) MW 2000



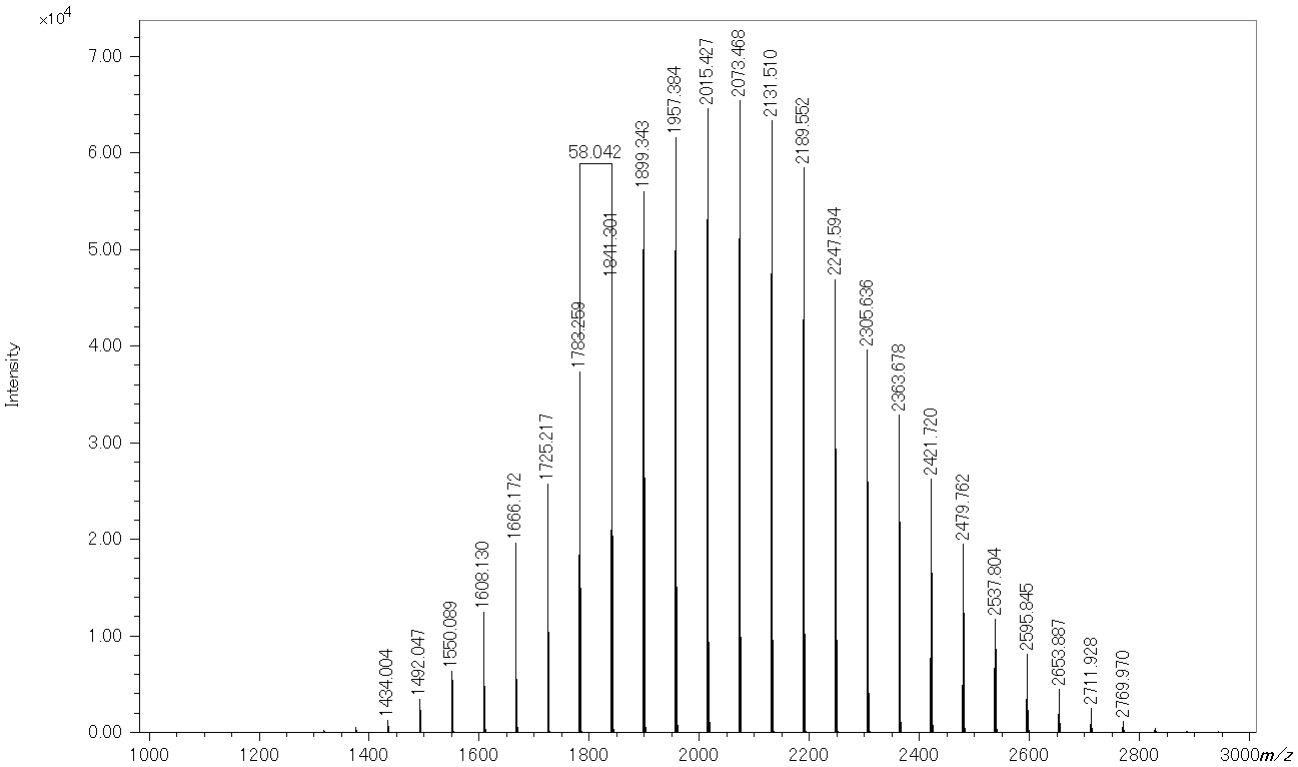
Structure	$HO(CH_2CH_2O)_nH$; $HO(C_2H_4O)_nH$
Ion Species	$[M+Na]^+$
Molecular weight Information	M_n 1,998; M_w 2,016; D 1.009
Matrix	CHCA
Cationization agent	NaTFA
Mode	SpiralTOF:Positive ion

PEO (poly(ethylene oxide)) MW 6000



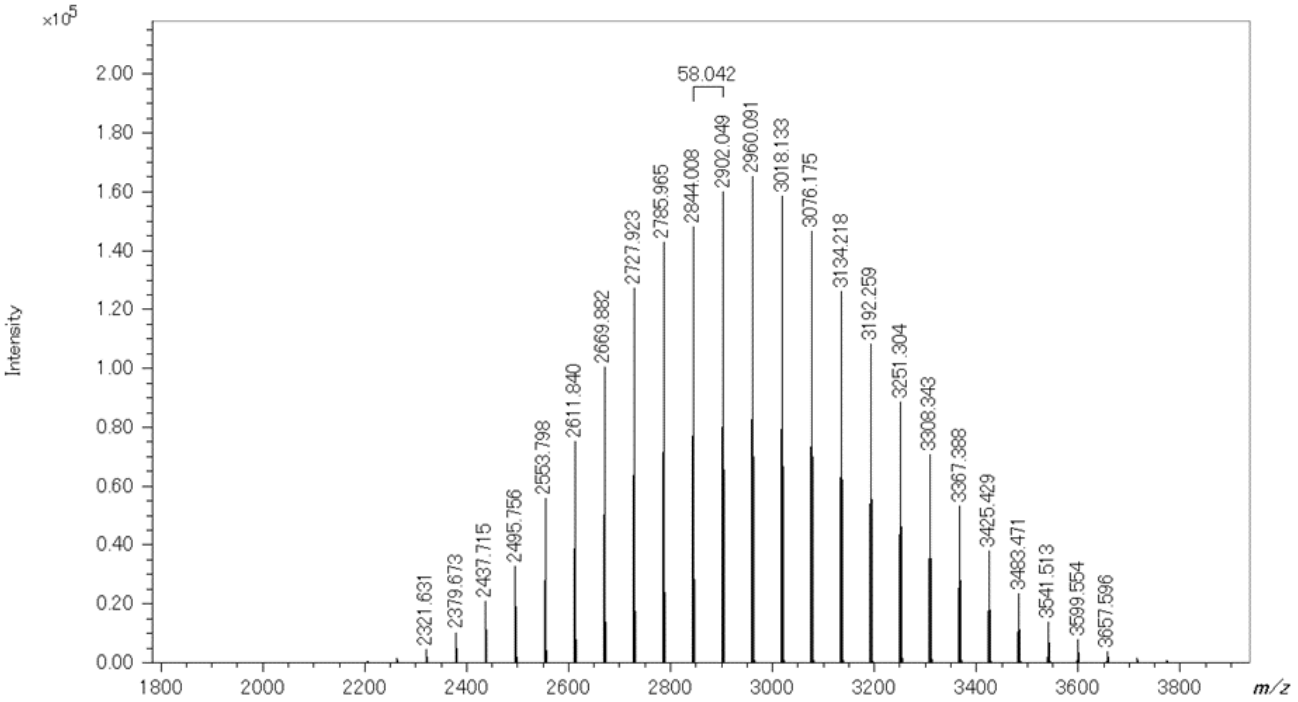
Structure	$HO(CH_2CH_2O)_nH$; $HO(C_2H_4O)_nH$
Ion Species	$[M+Na]^+$
Molecular weight Information	M_n 5,878; M_w 5,914; D 1.006
Matrix	DCTB
Cationization agent	NaTFA
Mode	SpiralTOF:Positive ion

PPO (poly(propylene oxide))



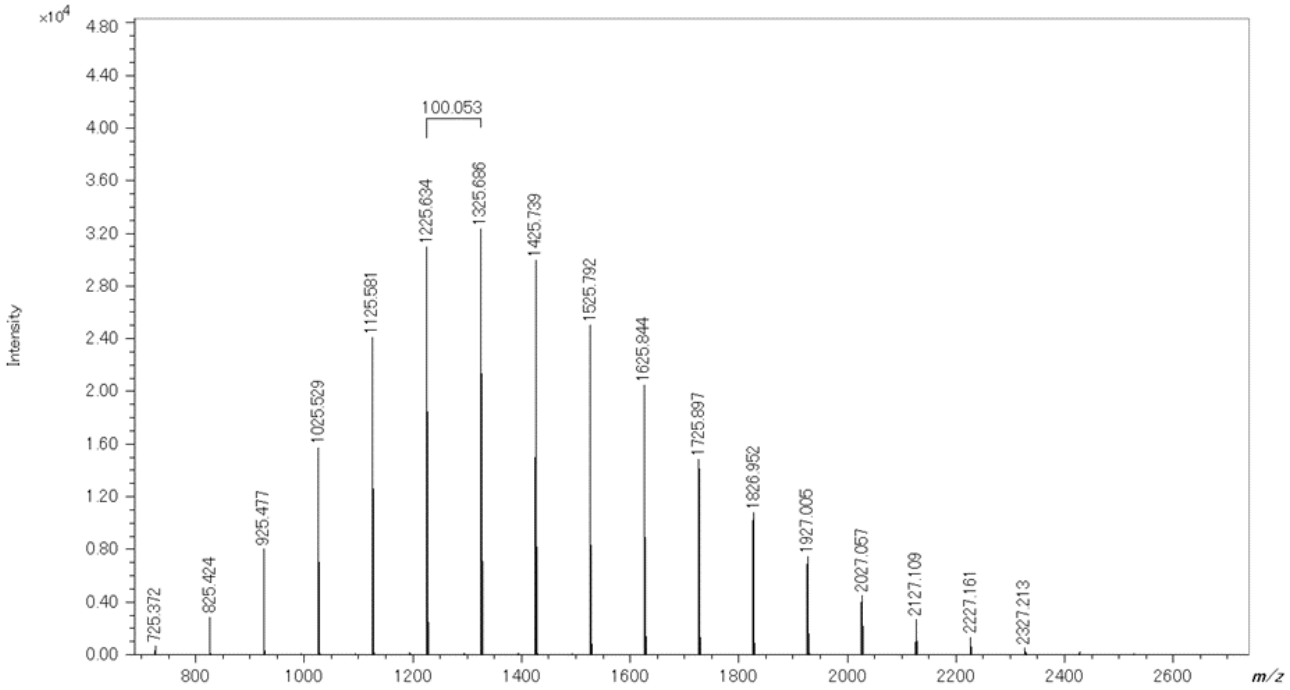
Structure	$HO[CH_2CH(CH_3)O]_nH$; $HO(C_3H_6O)_nH$
Ion Species	$[M+Na]^+$
Molecular weight Information	M_n 2,093; M_w 2,119; D 1.013
Matrix	DCTB
Cationization agent	NaTFA
Mode	SpiralTOF:Positive ion

PPO Triol (tris(polypropylene oxide) glyceryl ether)



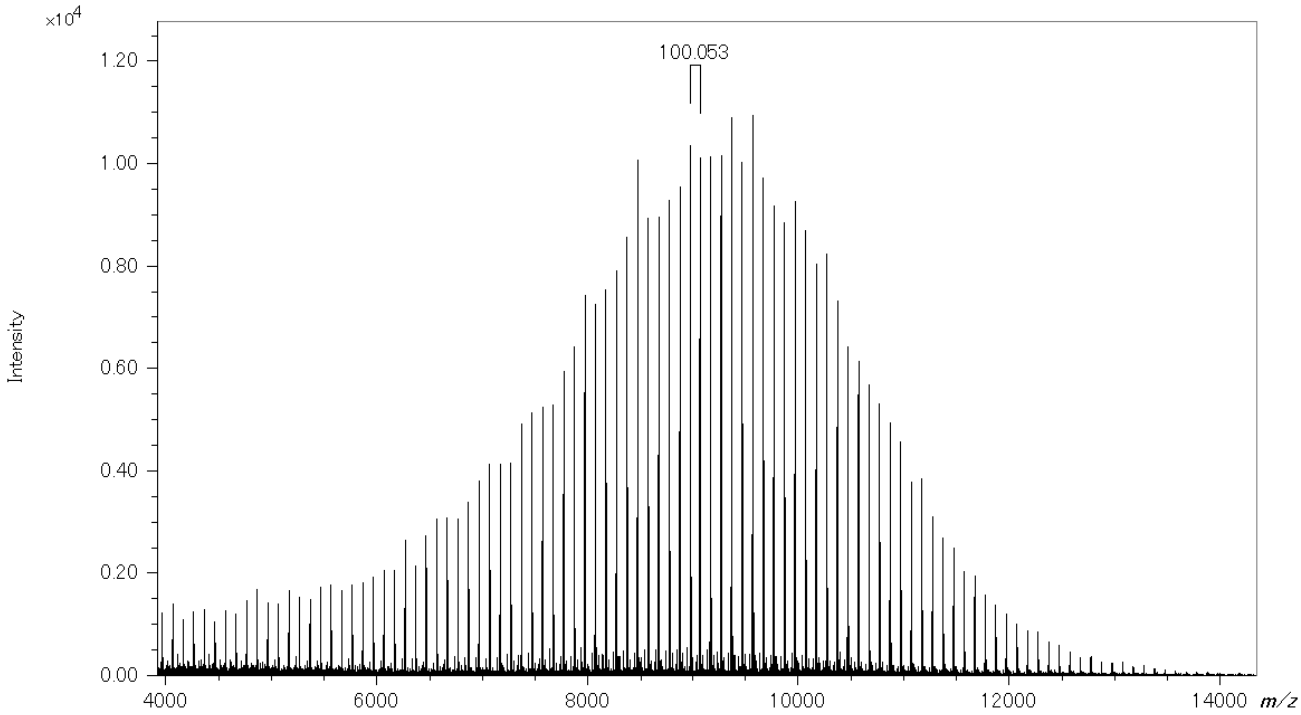
Structure	$HO(C_3H_6O)_nCH[CH_2(OC_3H_6)_nOH]_2$; $(C_3H_6O)_nC_3H_8O_3$
Ion Species	$[M+Na]^+$
Molecular weight Information	M_n 2,982; M_w 3,001; D 1.006
Matrix	DCTB
Cationization agent	NaTFA
Mode	SpiralTOF:Positive ion

PMMA (poly(methyl methacrylate))



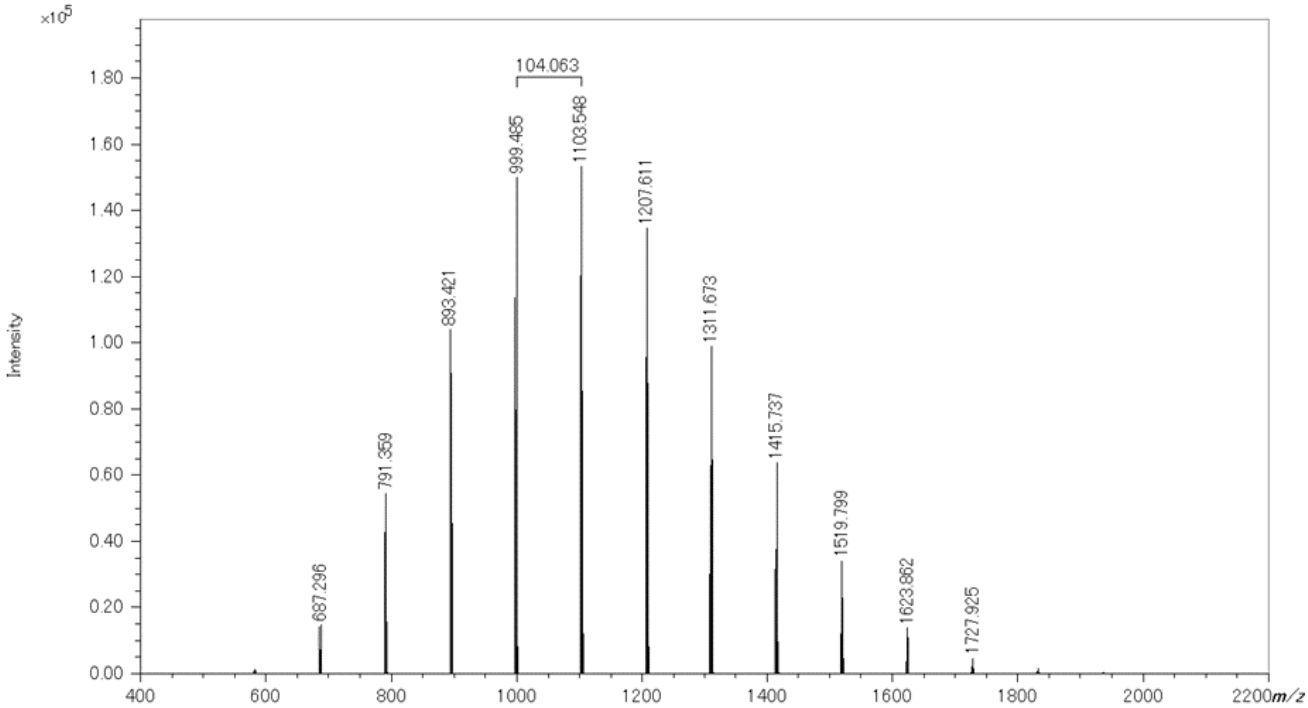
Structure	$H[CH_2C(CH_3)(CO_2CH_3)]_nH$; $H(C_5H_8O)_nH$
Ion Species	$[M+Na]^+$
Molecular weight Information	M_n 1,498; M_w 1,559; D 1.041
Matrix	DCTB
Cationization agent	NaTFA
Mode	SpiralTOF:Positive ion

PMMA (poly(methyl methacrylate))



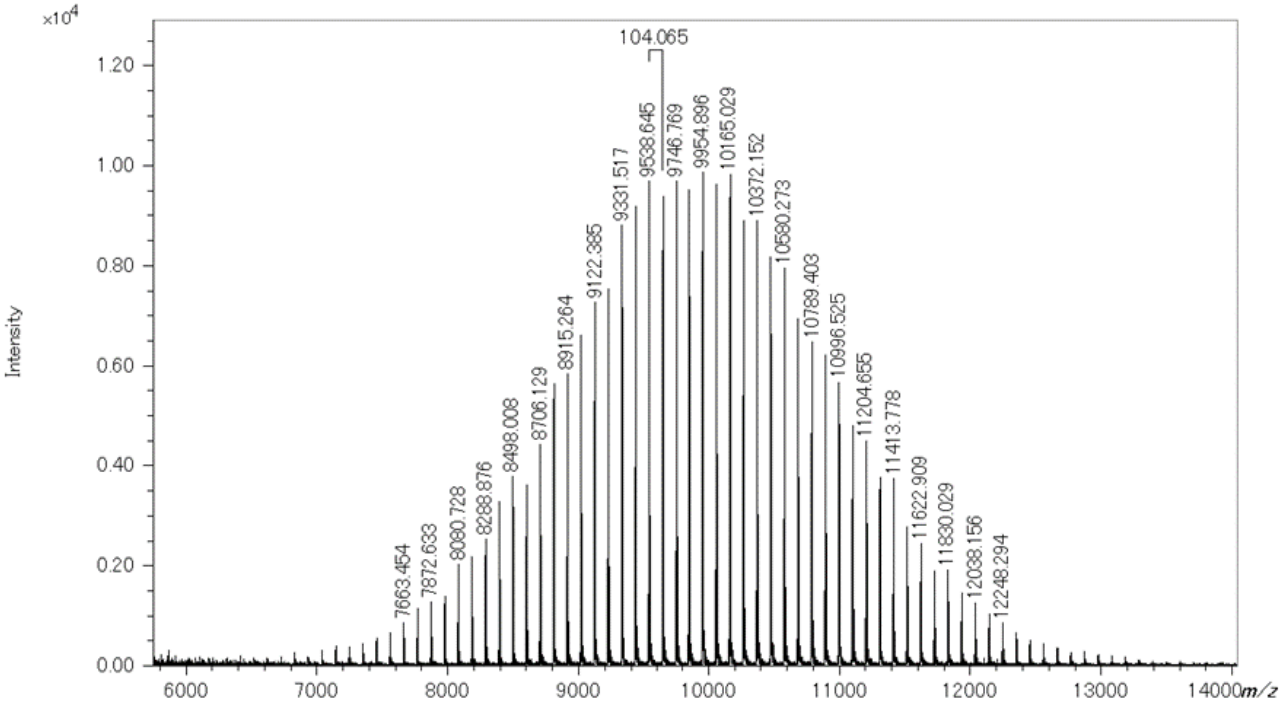
Structure	$-[CH_2C(CH_3)(CO_2CH_3)]_n-$; $-(C_5H_8O)_n-$
Ion Species	$[M+Na]^+$
Molecular weight Information	M_n 8,928; M_w 9,257; D 1.037
Matrix	DCTB
Cationization agent	NaTFA
Mode	SpiralTOF:Positive ion

PS (poly(styrene)) MW 1000



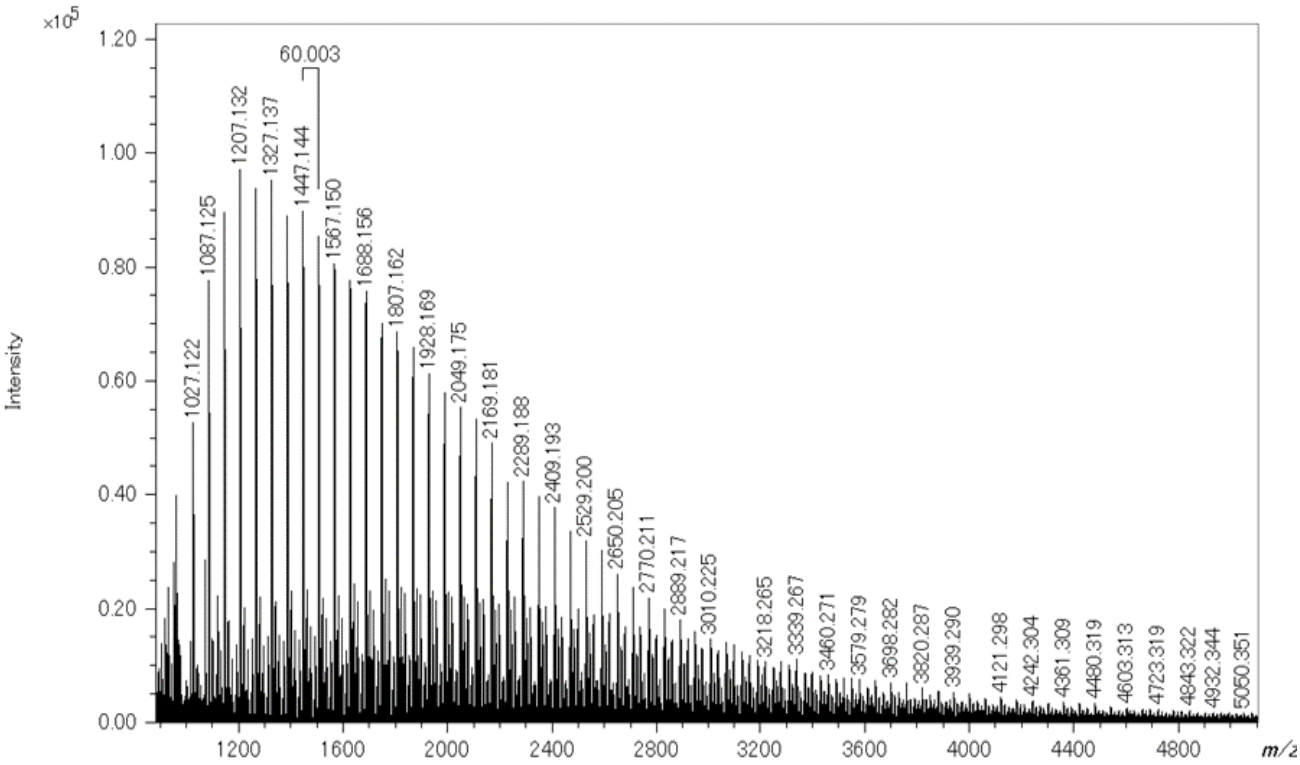
Structure	$H[CH_2CH(C_6H_5)]_nC4H9$; $H(C_8H_8)_nC_4H_9$
Ion Species	$[M+Ag]^+$
Molecular weight Information	M_n 1,157; M_w 1,196; D 1.033
Matrix	DCTB
Cationization agent	AgTFA
Mode	SpiralTOF:Positive ion

PS (poly(styrene)) MW 10000



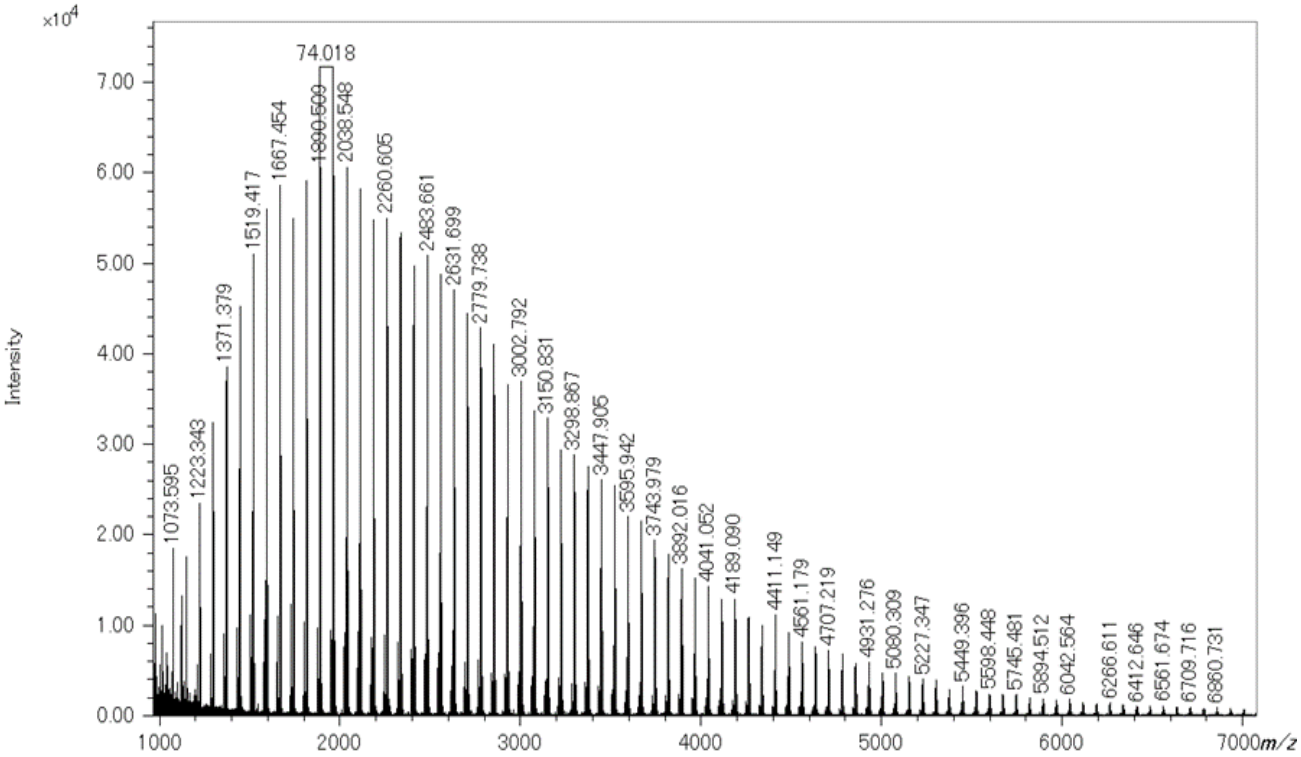
Structure	$H[CH_2CH(C_6H_5)]_nC4H9$; $H(C_8H_8)_nC_4H_9$
Ion Species	$[M+Ag]^+$
Molecular weight Information	M_n 9,998; M_w 10,119; D 1.012
Matrix	DCTB
Cationization agent	AgTFA
Mode	SpiralTOF:Positive ion

PMHS (poly(methylhydrosiloxane))



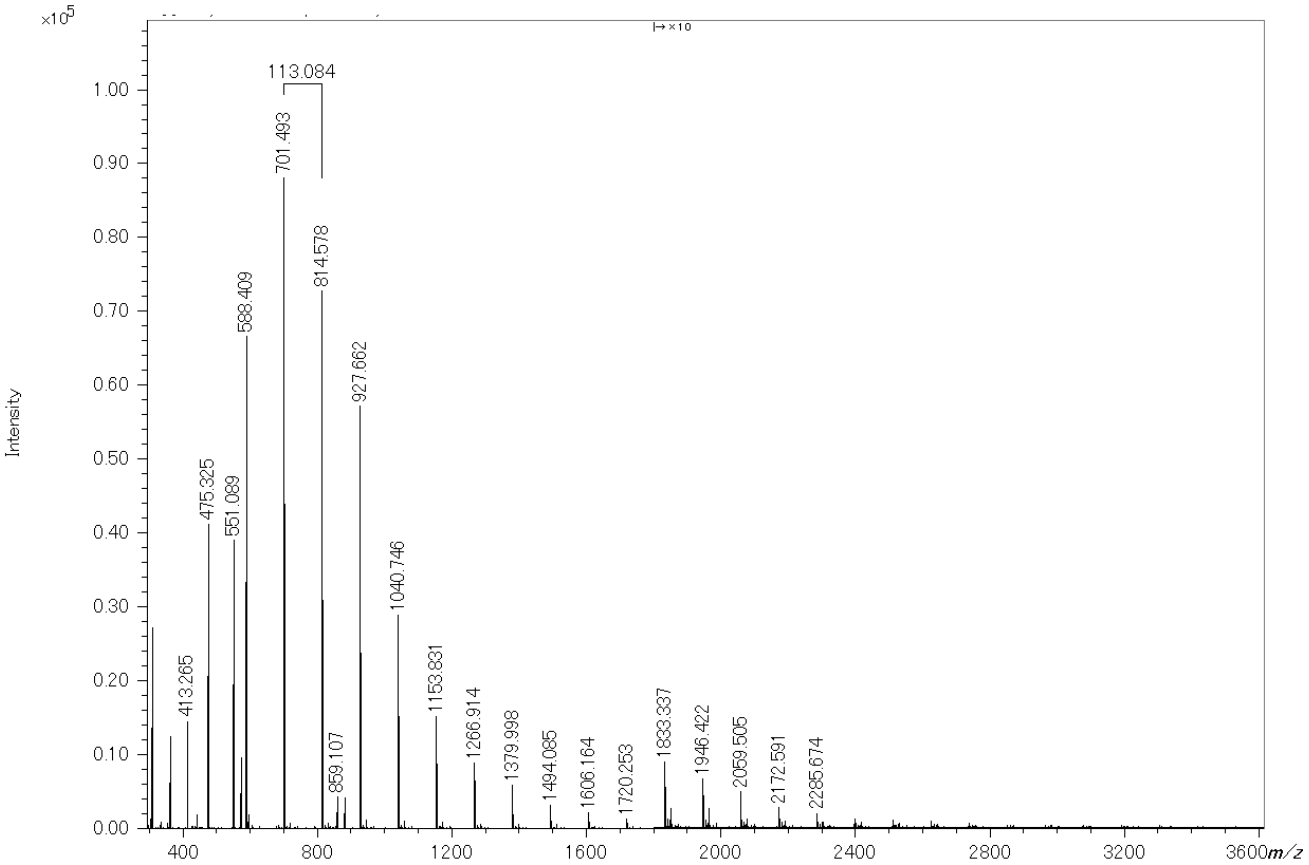
Structure	$(CH_3)_3SiO[(CH_3)HSiO]_nSi(CH_3)_3$; $(CH_4OSi)_nC_6H_{18}OSi_2$
Ion Species	$[M+Na]^+$
Molecular weight Information	M_n 2,123; M_w 2,602; D 1.226
Matrix	DCTB
Cationization agent	NaTFA
Mode	SpiralTOF:Positive ion

PDMS (poly(dimethylsiloxane))



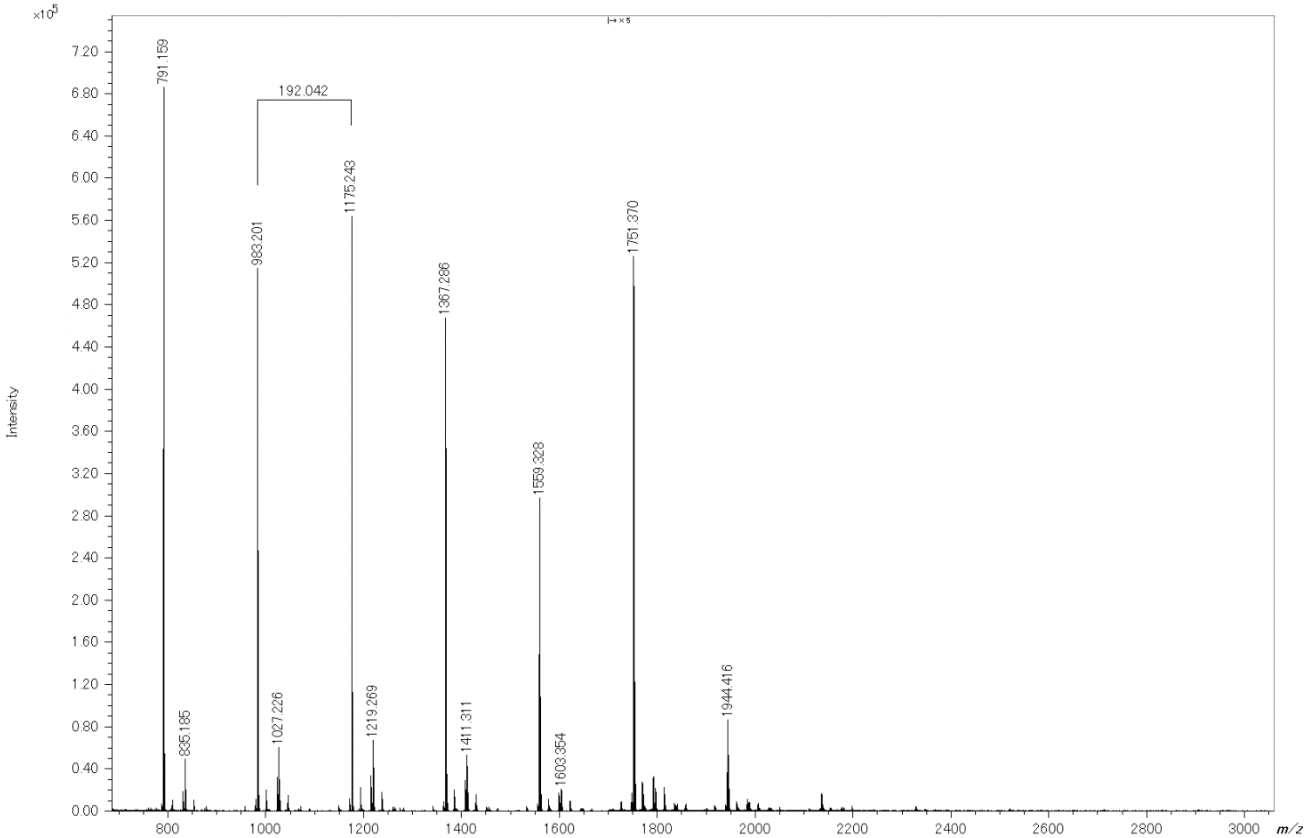
Structure	$-[(CH_3)_2SiO]_n-$; $-(C_2H_6SiO)_n-$
Ion Species	$[M+Na]^+$
Molecular weight Information	M_n 2,651; M_w 3,306; D 1.247
Matrix	DCTB
Cationization agent	NaTFA
Mode	SpiralTOF:Positive ion

Nylon 6 (polycaprolactam; poly(hexano-6-lactam))



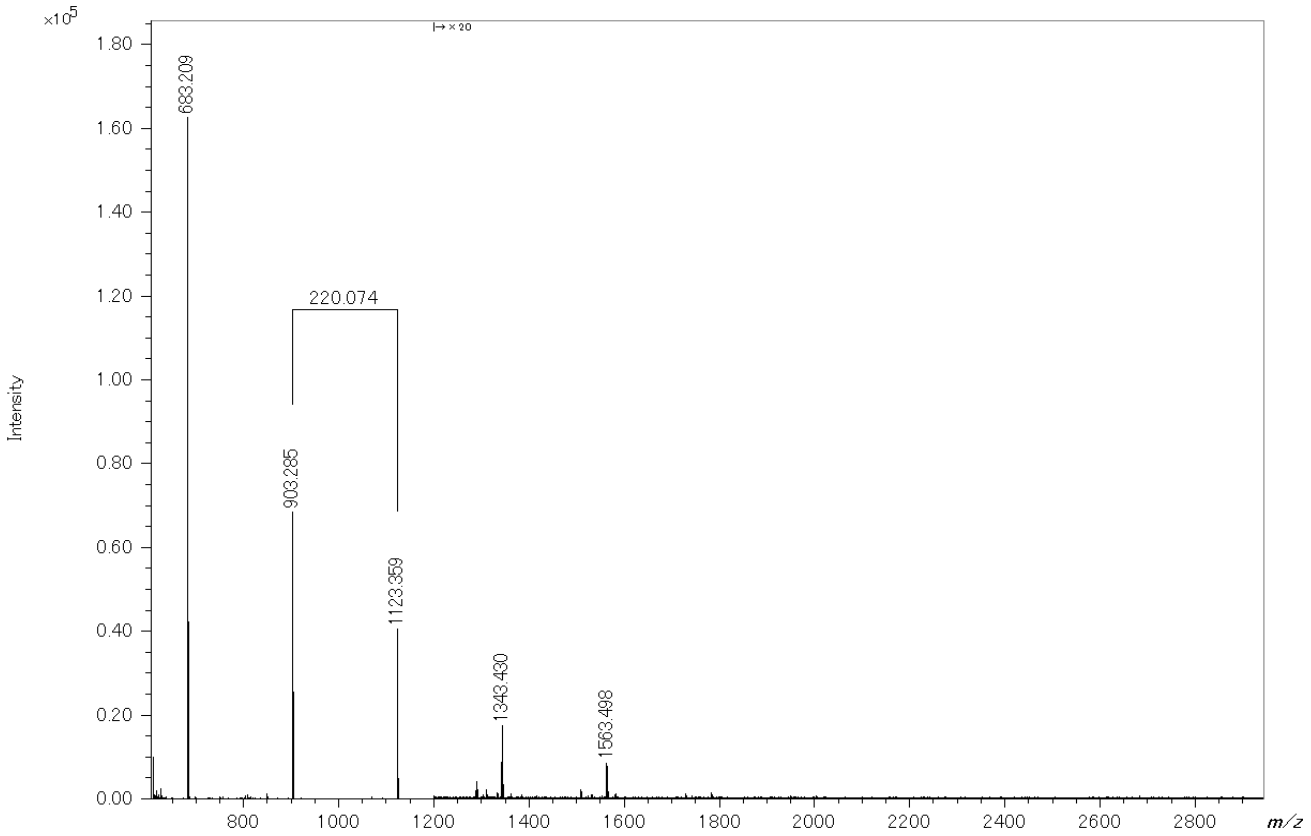
Structure	$-[NH(CH_2)_5CO]_n-$; $-(C_6H_{11}NO)_n-$
Ion Species	$[M+Na]^+$
Molecular weight Information	M_n 761; M_w 900; D 1.182
Matrix	HABA
Cationization agent	NaTFA
Mode	SpiralTOF:Positive ion

PET (poly(ethylene terephthalate)



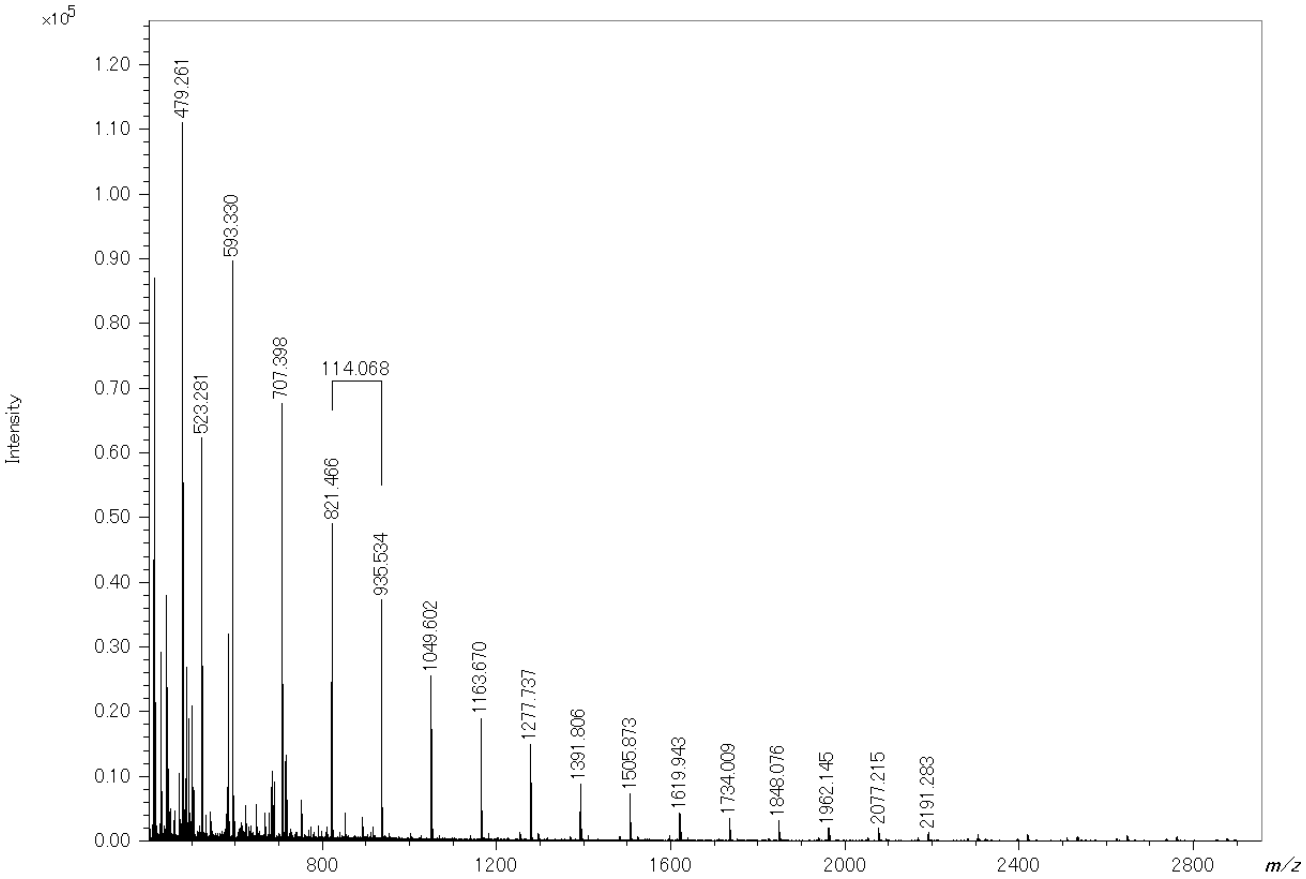
Structure	$-[COO(C_6H_4)COO(CH_2)_2]_n-$; $-(C_{10}H_8O_4)_n-$
Ion Species	$[M+Na]^+$
Molecular weight Information	M_n 1203, M_w 1281, D 1.065
Matrix	THAP
Cationization agent	NaTFA
Mode	SpiralTOF:Positive ion

PBT (poly(butylene terephthalate))



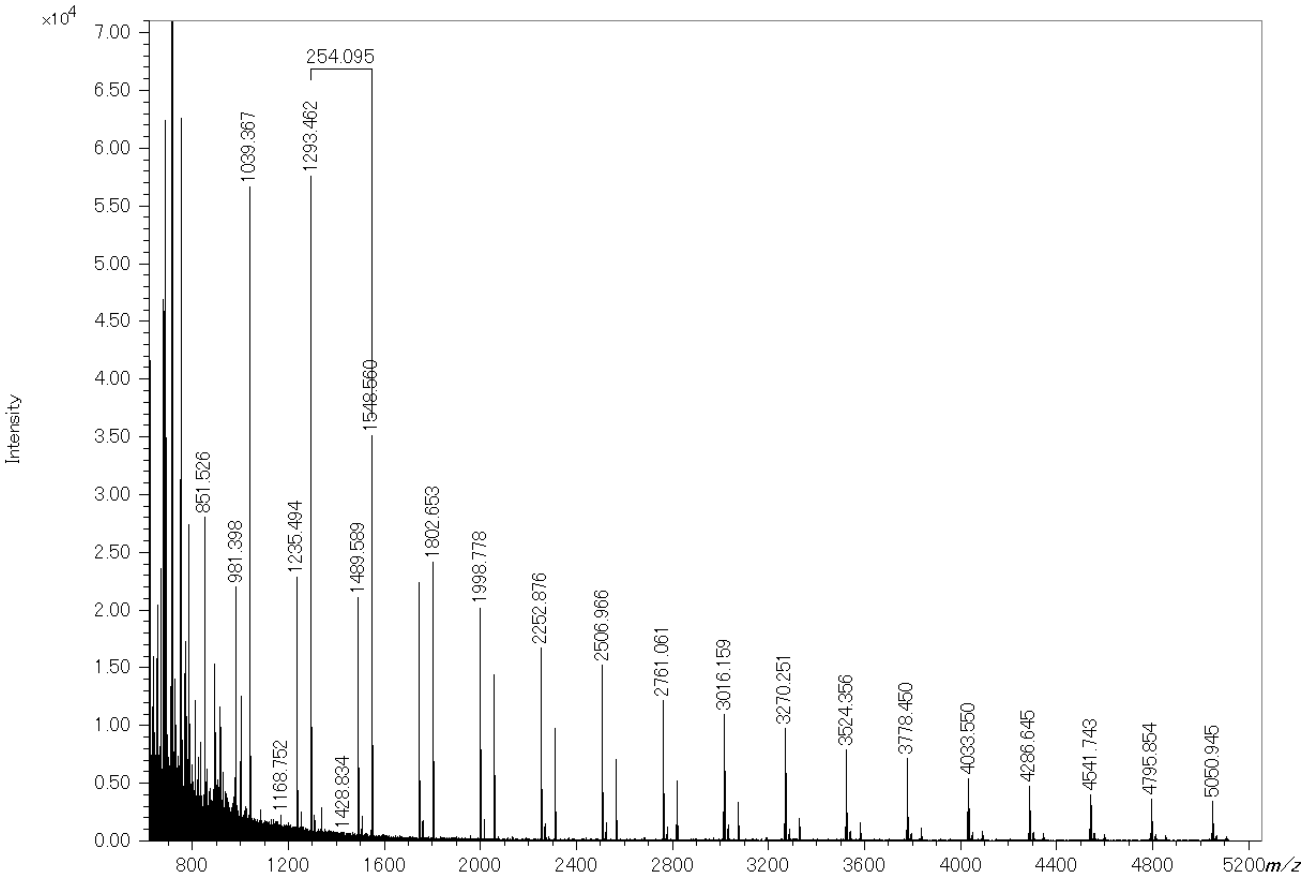
Structure	$-[CO(C_6H_4)COO(CH_2)_4O]_n-$; $-(C_{12}H_{14}O_4)_n-$
Ion Species	$[M+Na]^+$
Molecular weight Information	M_n 790; M_w 852; D 1.079
Matrix	DHB
Cationization agent	NaTFA
Mode	SpiralTOF:Positive ion

PCL (poly(caprolactone))



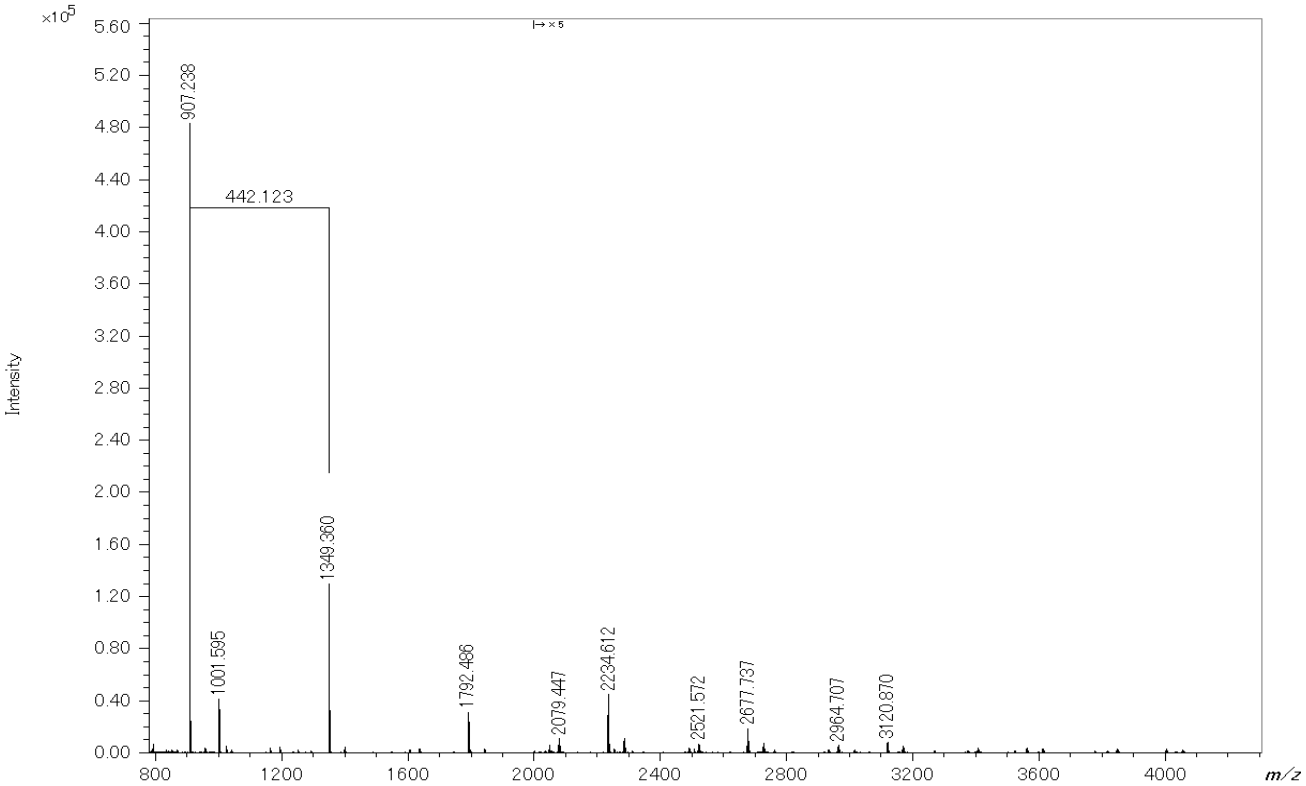
Structure	$-[O(CH_2)_5CO]_n-$; $-(C_6H_{10}O_2)_n-$
Ion Species	$[M+Na]^+$
Molecular weight Information	M_n 915; M_w 1,268; D 1.386
Matrix	DCTB
Cationization agent	NaTFA
Mode	SpiralTOF:Positive ion

PC (polycarbonate)



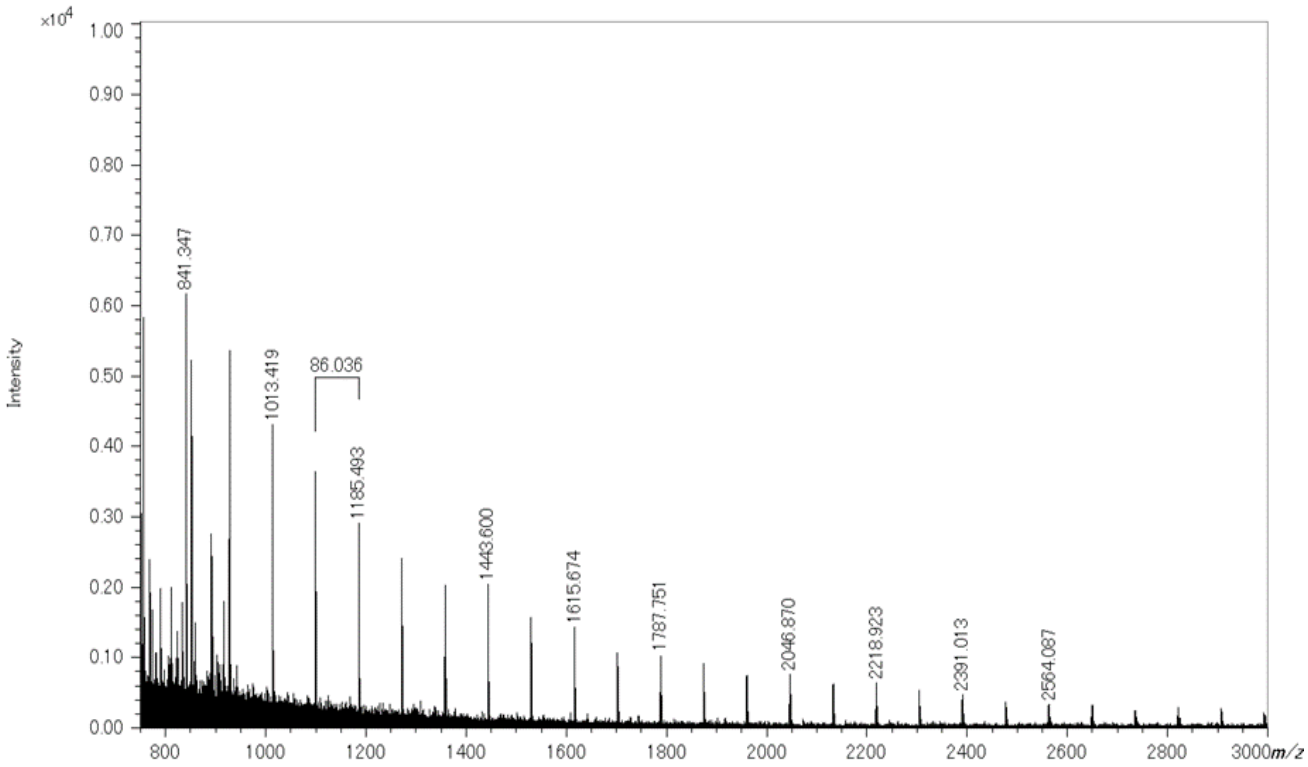
Structure	$-[O(C_6H_4)C(CH_3)_2(C_6H_4)OCO]_n-$; $-(C_{16}H_{14}O_3)_n-$
Ion Species	$[M+Na]^+$
Molecular weight Information	M_n 2,522; M_w 3,113; D 1.236
Matrix	DCTB
Cationization agent	NaTFA
Mode	SpiralTOF:Positive ion

PSF (polysulfone)



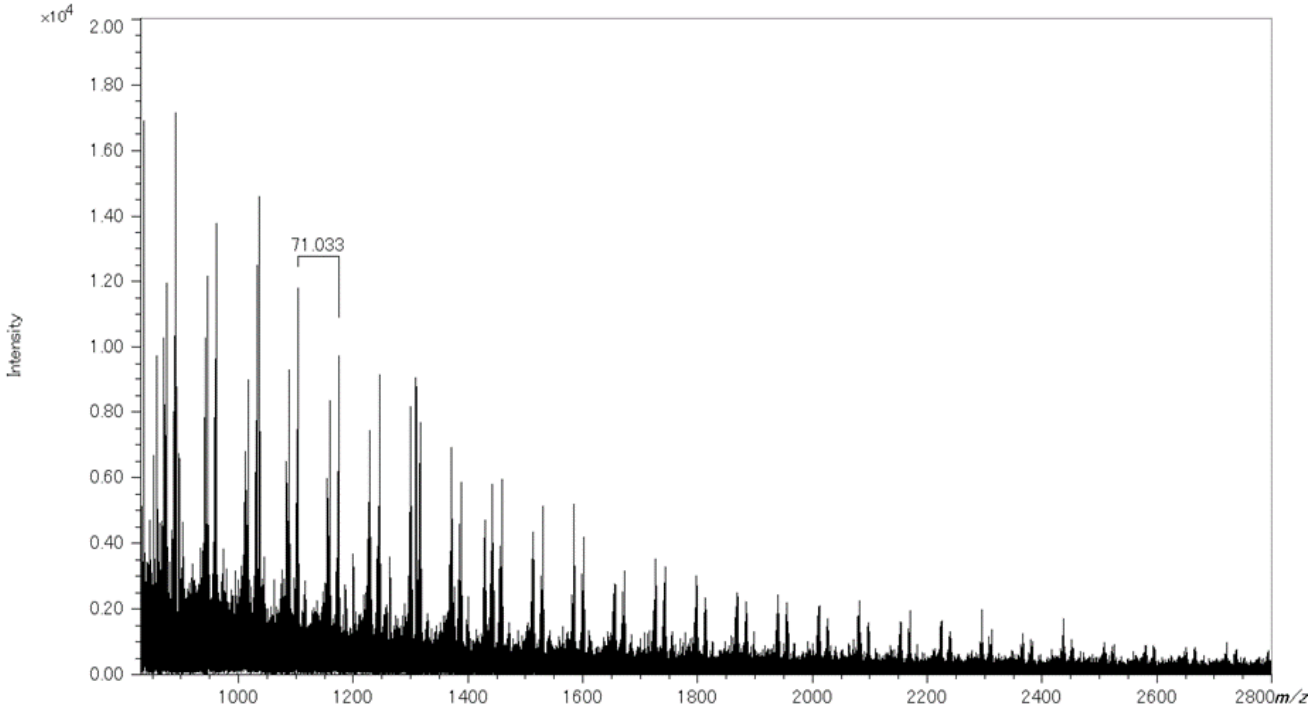
Structure	$-[(C_6H_4)C(CH_3)_2(C_6H_4)O(C_6H_4)SO_2(C_6H_4)O]_n-$; $-(C_{27}H_{22}SO_4)_n-$
Ion Species	$[M+Na]^+$
Molecular weight Information	M_n 1,294; M_w 1,559; D 1.205
Matrix	DCTB
Cationization agent	NaTFA
Mode	SpiralTOF:Positive ion

PVAc (polyvinyl acetate; poly(ethenyl ethanoate))



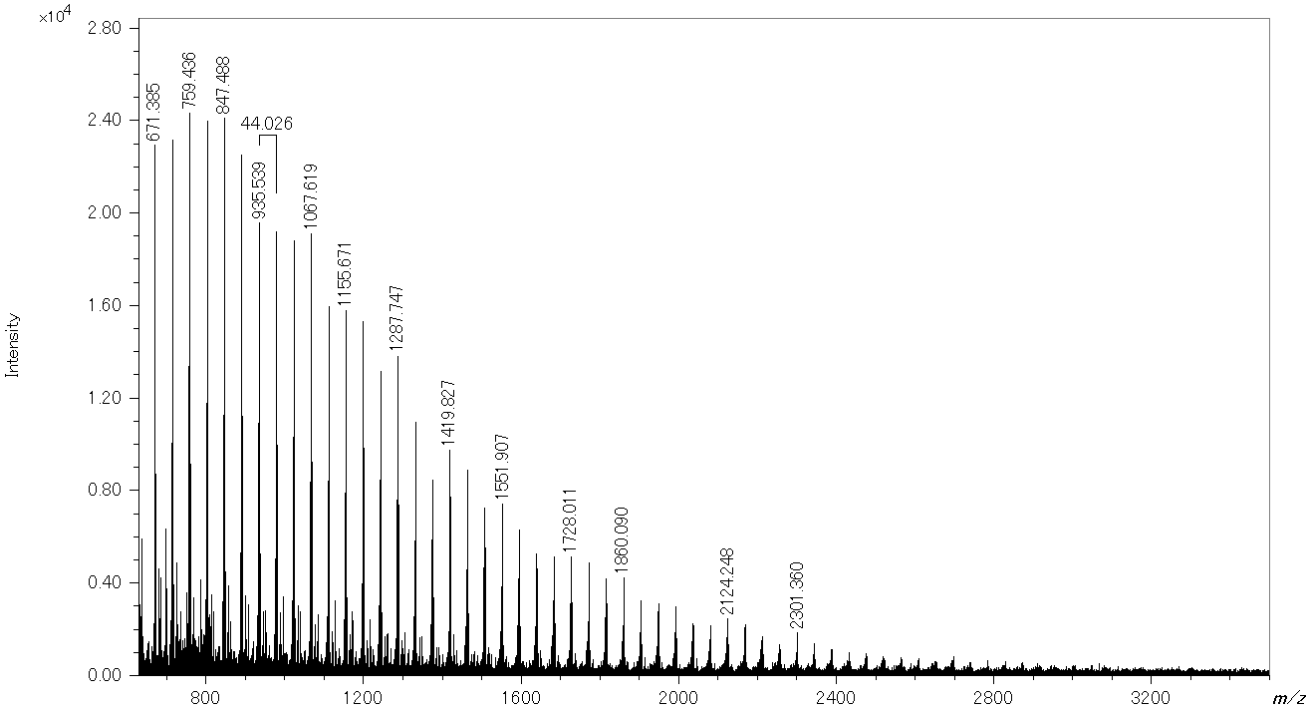
Structure	$-[CH_2CH(O_2CCH_3)]_n-$; $-(C_4H_6O_2)_n-$
Ion Species	$[M+Na]^+$
Molecular weight Information	M_n 1,612; M_w 1,818; D 1.128
Matrix	DCTB
Cationization agent	NaTFA
Mode	SpiralTOF:Positive ion

PPA (polyacrylamide; poly(2-propenamide))



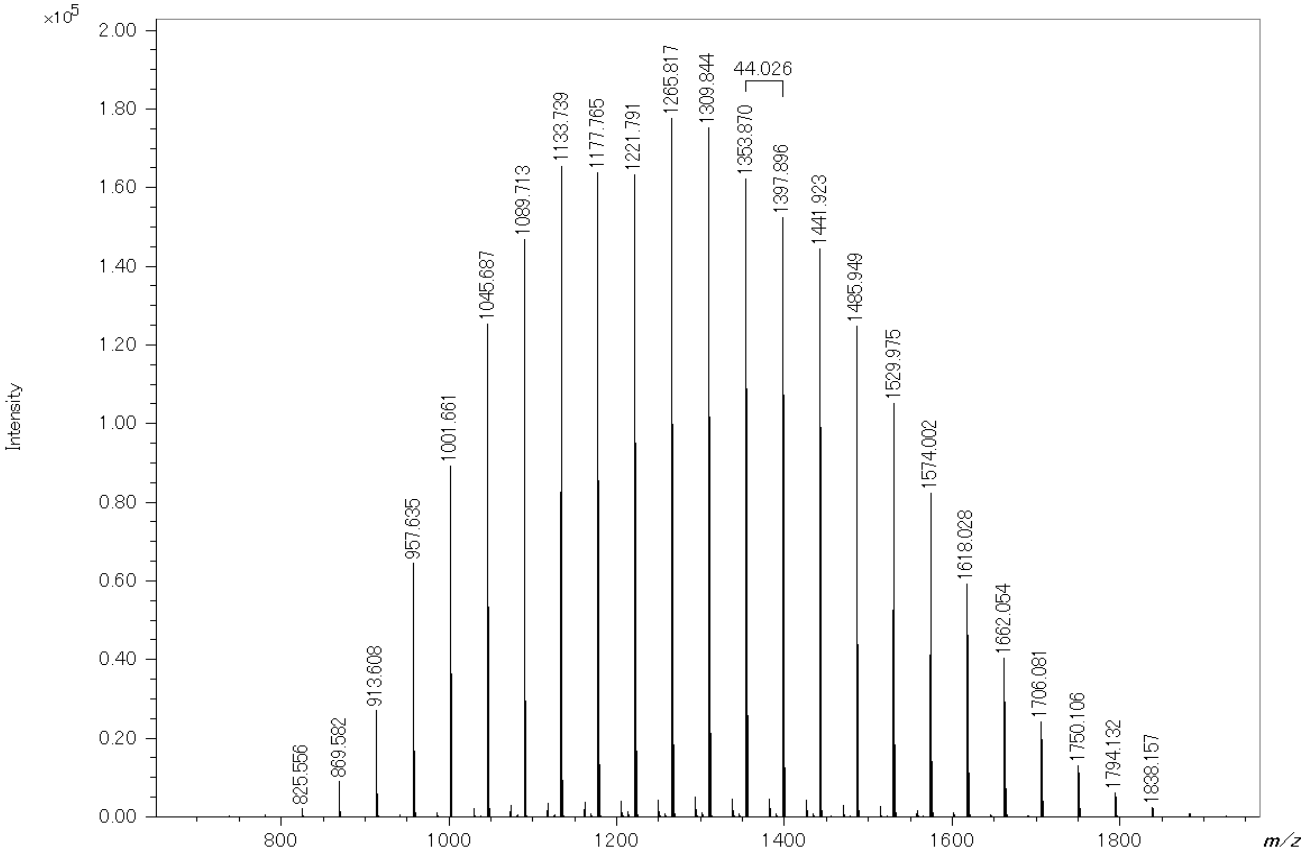
Structure	$-[CH_2CH(CONH_2)]_n-$; $-(C_3H_5NO)_n-$
Ion Species	$[M+Na]^+$
Molecular weight Information	
Matrix	DHB
Cationization agent	NaTFA
Mode	SpiralTOF:Positive ion

PVA (poly(vinyl alcohol))



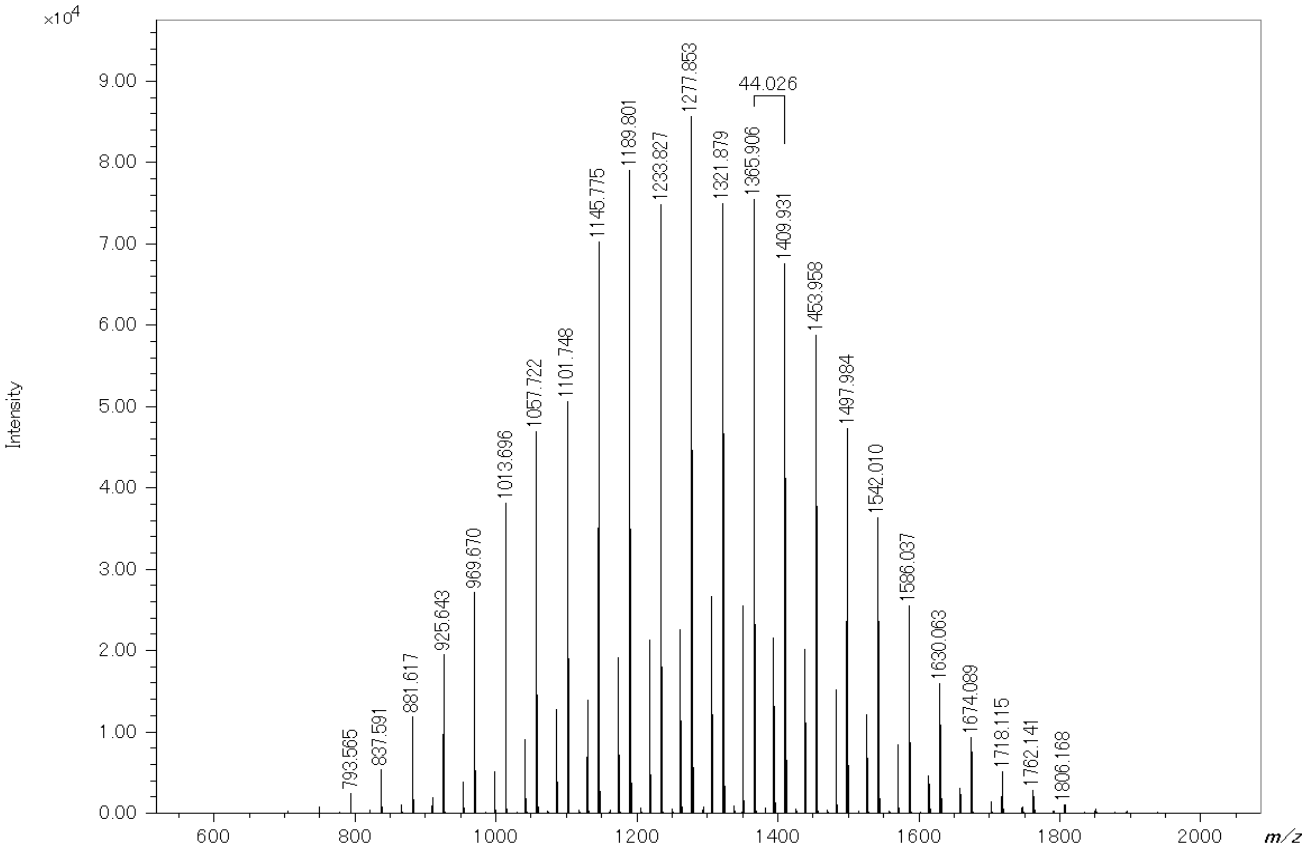
Structure	$-[CH_2CH(OH)]_n-$; $-(C_2H_4O)_n-$
Ion Species	$[M+Na]^+$
Molecular weight Information	M_n 1,222; M_w 1,526; D 1.249
Matrix	DHB
Cationization agent	NaTFA
Mode	SpiralTOF:Positive ion

Polyethylene glycol monododecyl ether



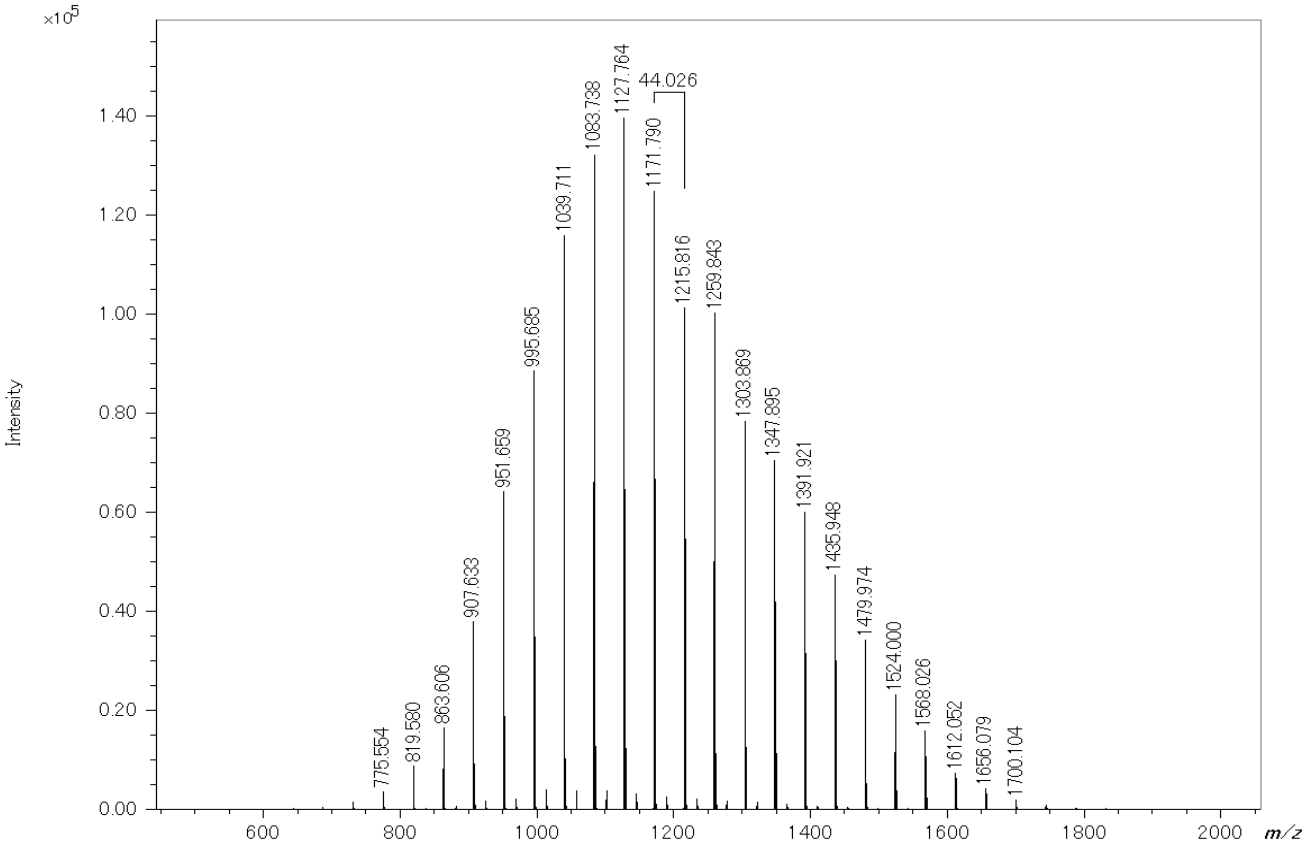
Structure	$HO[(CH_2)_2O]_n(CH_2)_{11}CH_3$; $HO(C_2H_4O)_nC_{12}H_{25}$
Ion Species	$[M+Na]^+$
Molecular weight Information	M_n 1,331; M_w 1,359; D 1.021
Matrix	DCTB
Cationization agent	NaTFA
Mode	SpiralTOF:Positive ion

Polyethylene glycol monocetyl ether



Structure	$HO[(CH_2)_2O]_n(CH_2)_{15}CH_3$; $HO(C_2H_4O)_nC_{16}H_{33}$
Ion Species	$[M+Na]^+$
Molecular weight Information	M_n 1,312; M_w 1,332; D 1.016
Matrix	DCTB
Cationization agent	NaTFA
Mode	SpiralTOF:Positive ion

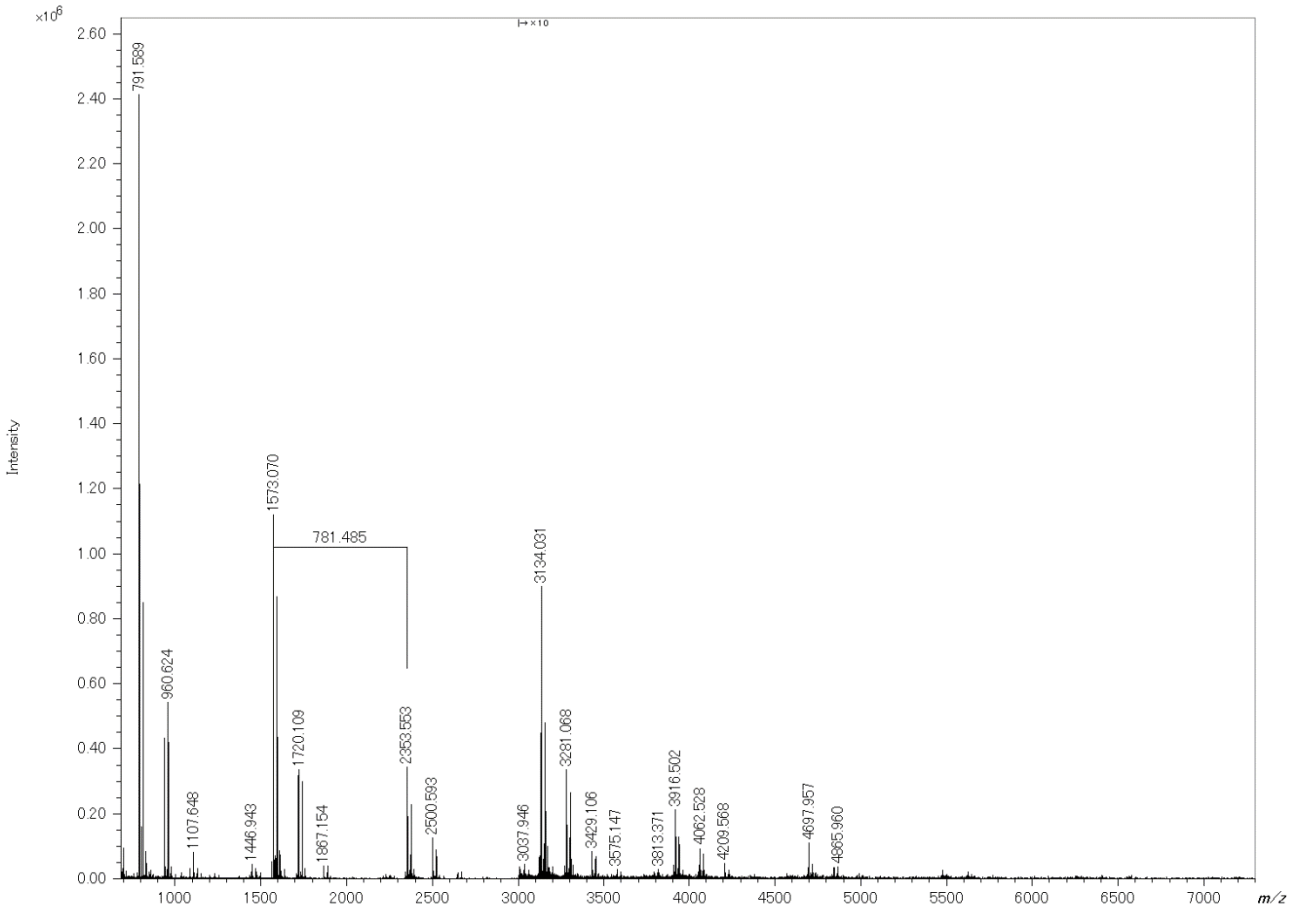
Polyethylene glycol monooleyl ether



Structure	$HO[(CH_2)_2O]_n(CH_2)_{17}CH_3$; $HO(C_2H_4O)C_{18}H_{35}$
Ion Species	$[M+Na]^+$
Molecular weight Information	M_n 1,172; M_w 1,196; D 1.021
Matrix	DCTB
Cationization agent	NaTFA
Mode	SpiralTOF:Positive ion

ADK STAB LA-68

(High molecular weight HALS (hindered amine light stabilizer))

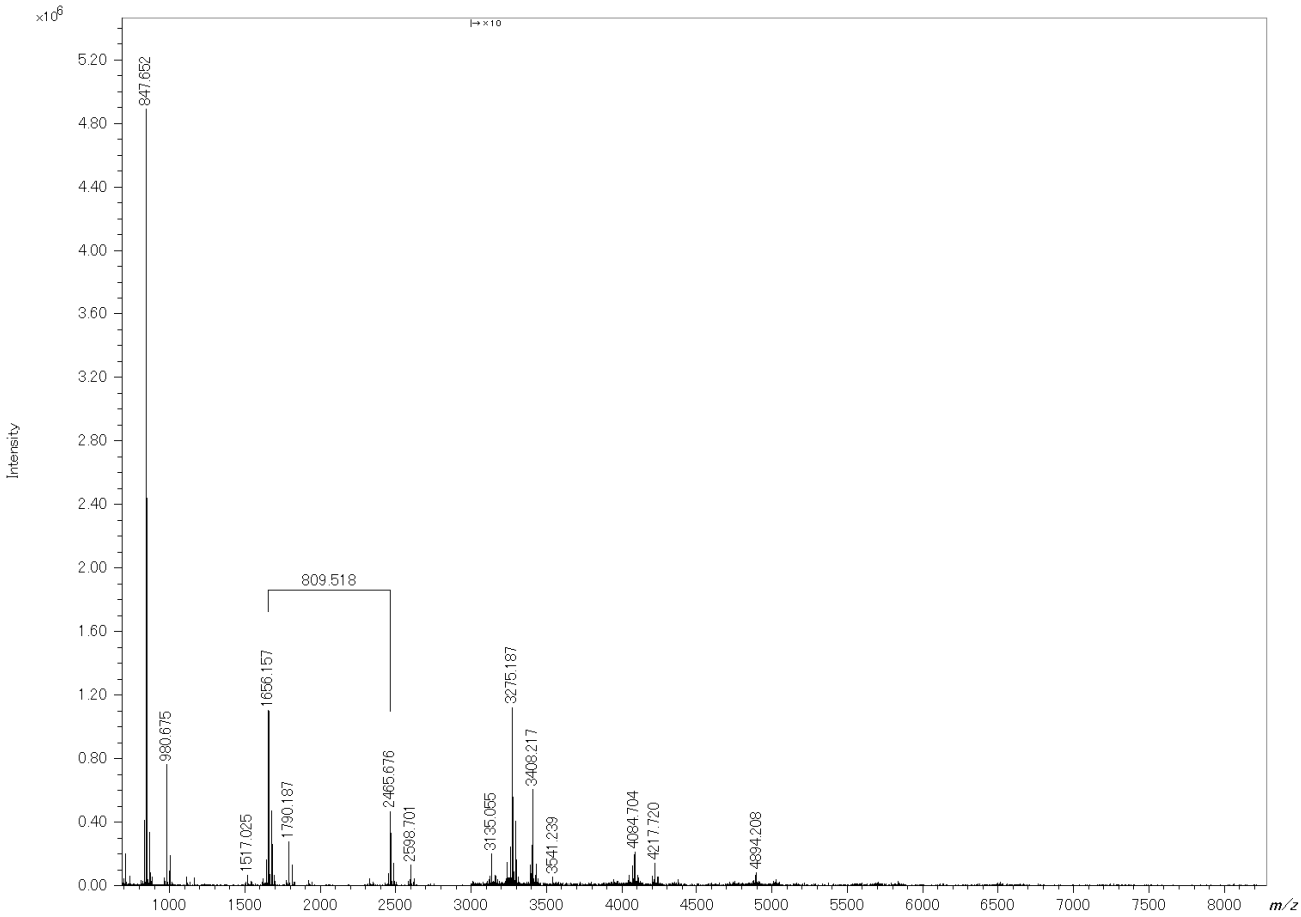


Structure	$C_9H_{18}N[C_{41}H_{68}N_2O_{12}]_n$-$C_{35}H_{60}O_8N_3$
Ion Species	$[M+H]^+$, $[M+Na]^+$
Molecular weight Information	M_n 1298, M_w 1538, D 1.202
Matrix	DHB
Cationization agent	None
Mode	SpiralTOF:Positive ion

* ADK STAB is either a registered trademark or a trademark of ADEKA Corporation in Japan and/or other countries.

ADK STAB LA-63P

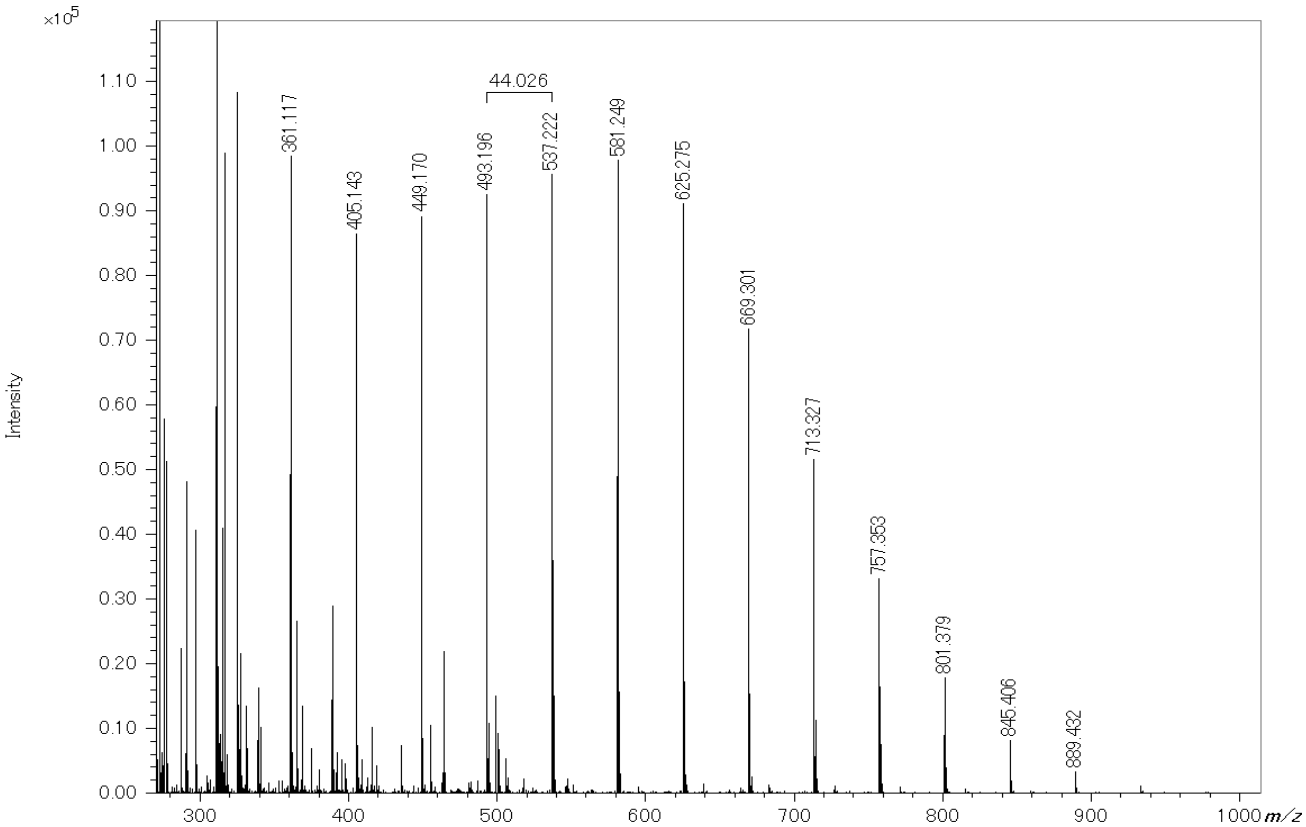
(High molecular weight HALS (hindered amine light stabilizer))



Structure	$C_{10}H_{20}N[C_{43}H_{72}N_2O_{12}]_n$-$C_{38}H_{66}O_8N_3$
Ion Species	$[M+H]^+$, $[M+Na]^+$
Molecular weight Information	M_n 1157, M_w 1424, D 1.231
Matrix	DHB
Cationization agent	None
Mode	SpiralTOF:Positive ion

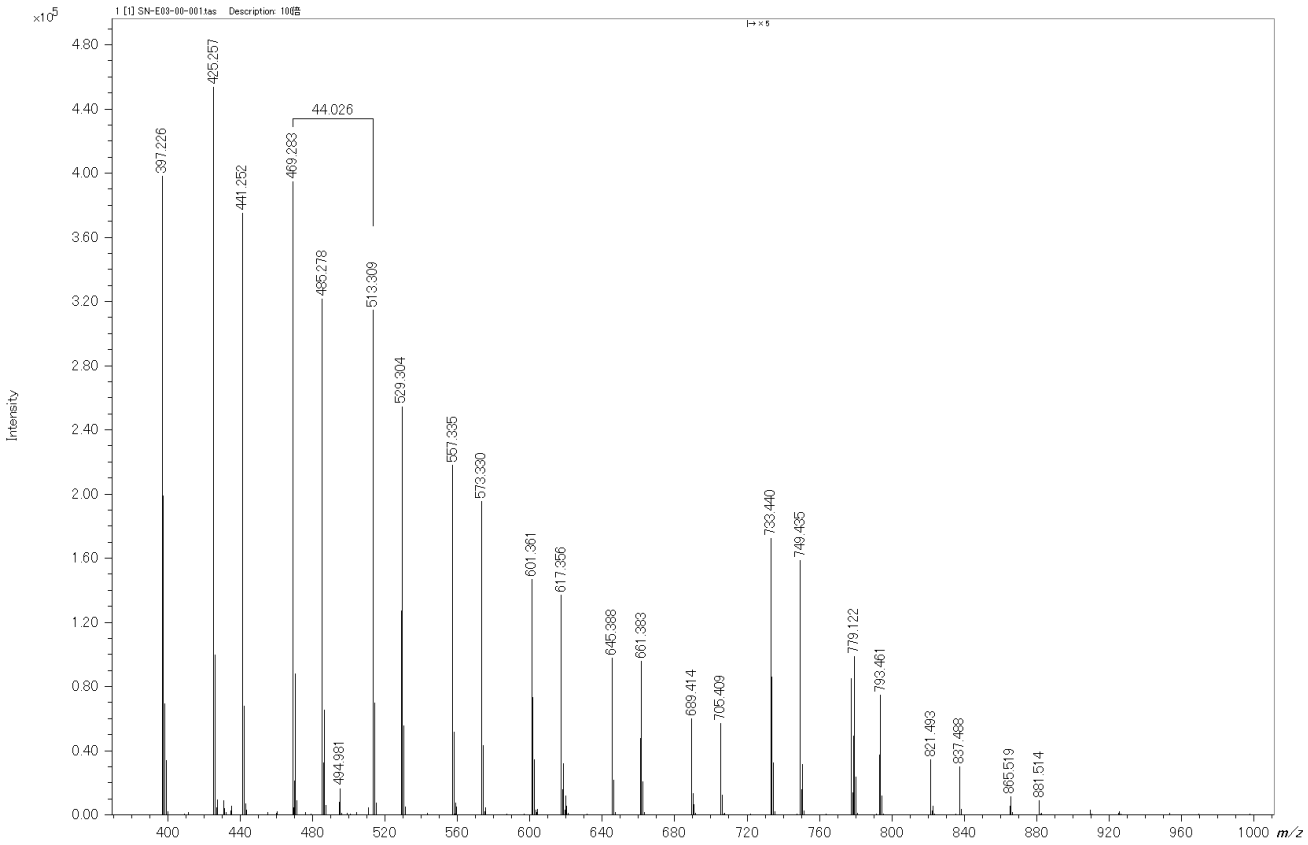
* ADK STAB is either a registered trademark or a trademark of ADEKA Corporation in Japan and/or other countries.

Polyethylene glycol sulfate



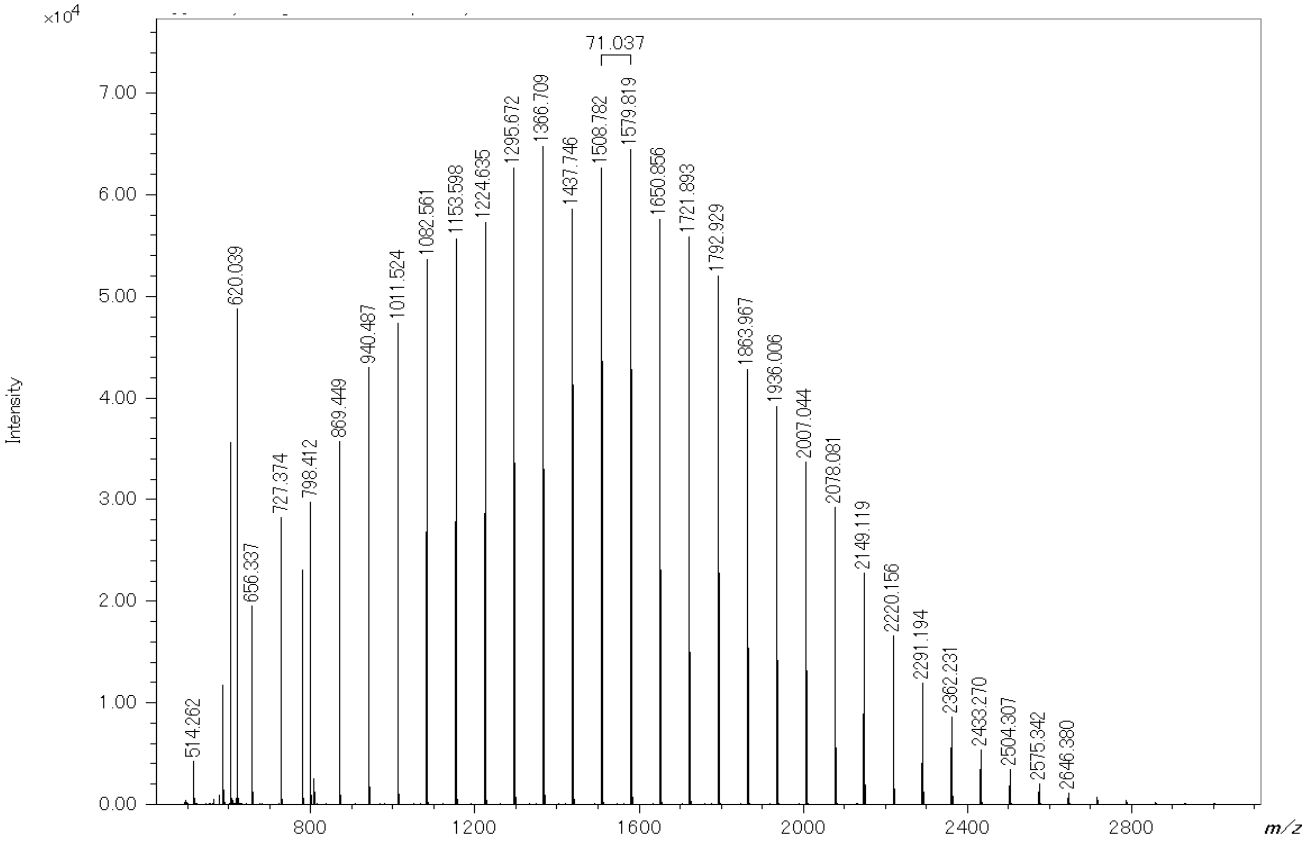
Structure	$HO[(CH_2)_2O]_nSO_3H$; $HO(C_2H_4O)_nSO_3H$
Ion Species	$[M-H]^-$
Molecular weight Information	M_n 535; M_w 573; D 1.070
Matrix	DCTB
Cationization agent	None
Mode	SpiralTOF:Negative ion

Polyoxyethylene alkyl ether sulfuric acid



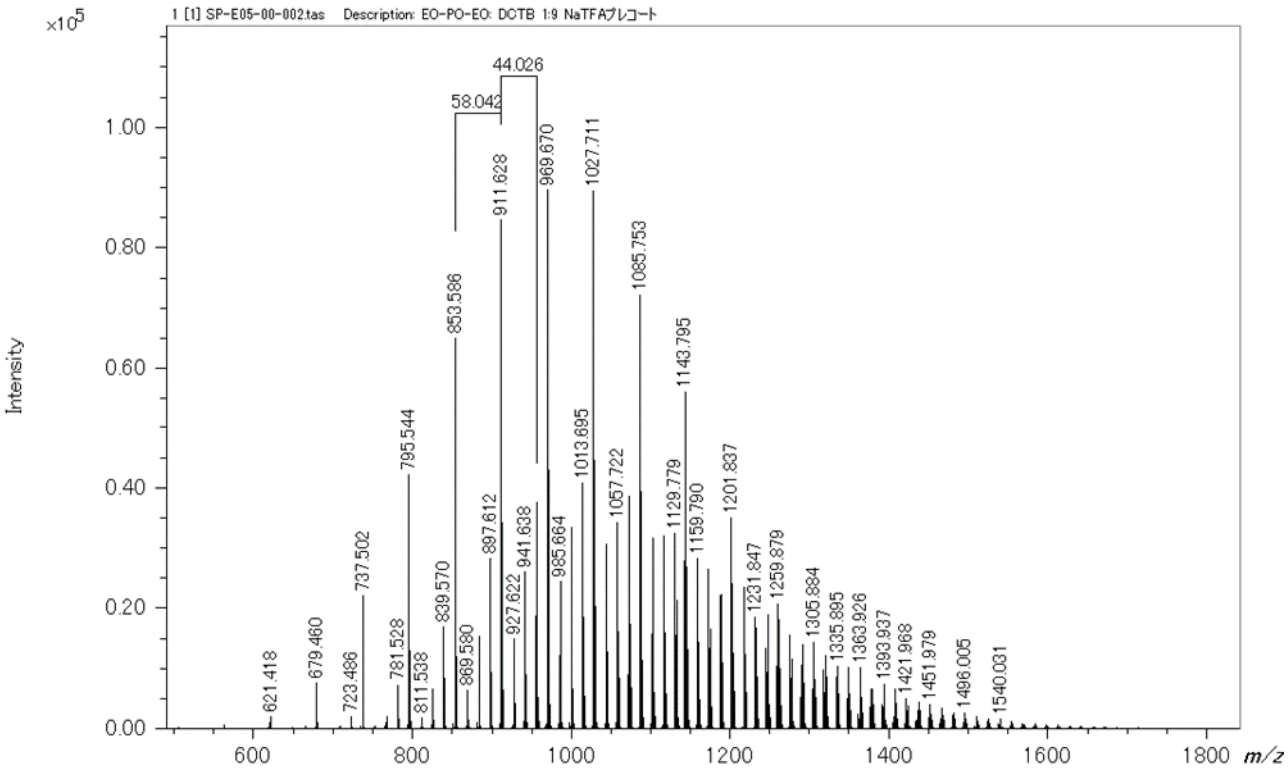
Structure	$NaSO_3[(CH_2)_2O]_nO(CH_2)_{11}CH_3$; $NaSO_3(C_2H_4O)_nOC_{12}H_{25}$ $NaSO_3[(CH_2)_2O]_nO(CH_2)_{13}CH_3$; $NaSO_3(C_2H_4O)_nOC_{14}H_{29}$
Ion Species	$[M-Na]^-$
Molecular weight Information	M_n 511, M_w 527, D 1.032
Matrix	CHCA
Cationization agent	None
Mode	SpiralTOF:Negative ion

Poly(alanine)

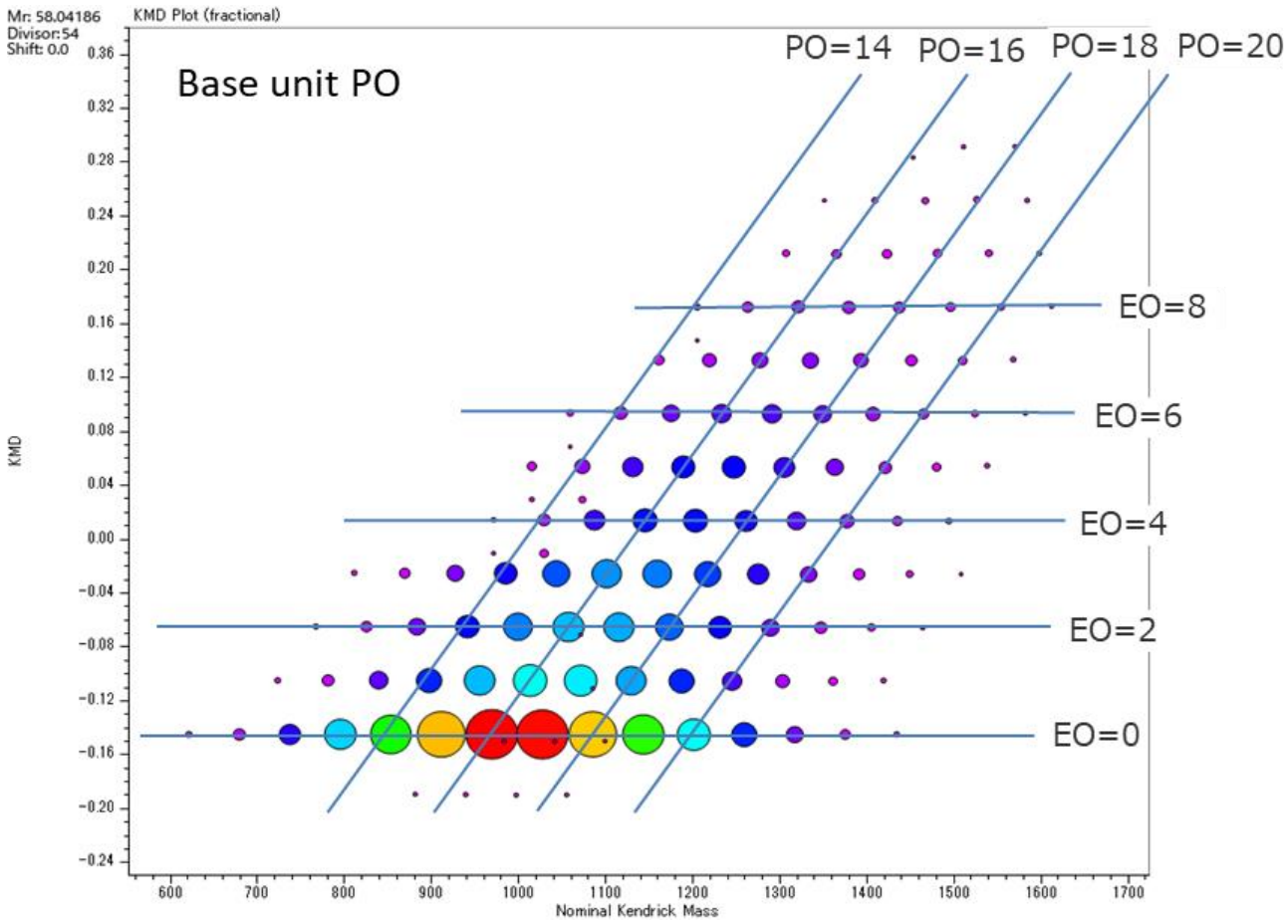


Structure	$H[NHCH(CH_3)CO]_nOH$; $H(C_3H_5NO)_nOH$
Ion Species	$[M-H]^-$
Molecular weight Information	M_n 1,652; M_w 1,765; D 1.069
Matrix	DCTB
Cationization agent	None
Mode	SpiralTOF:Negative ion

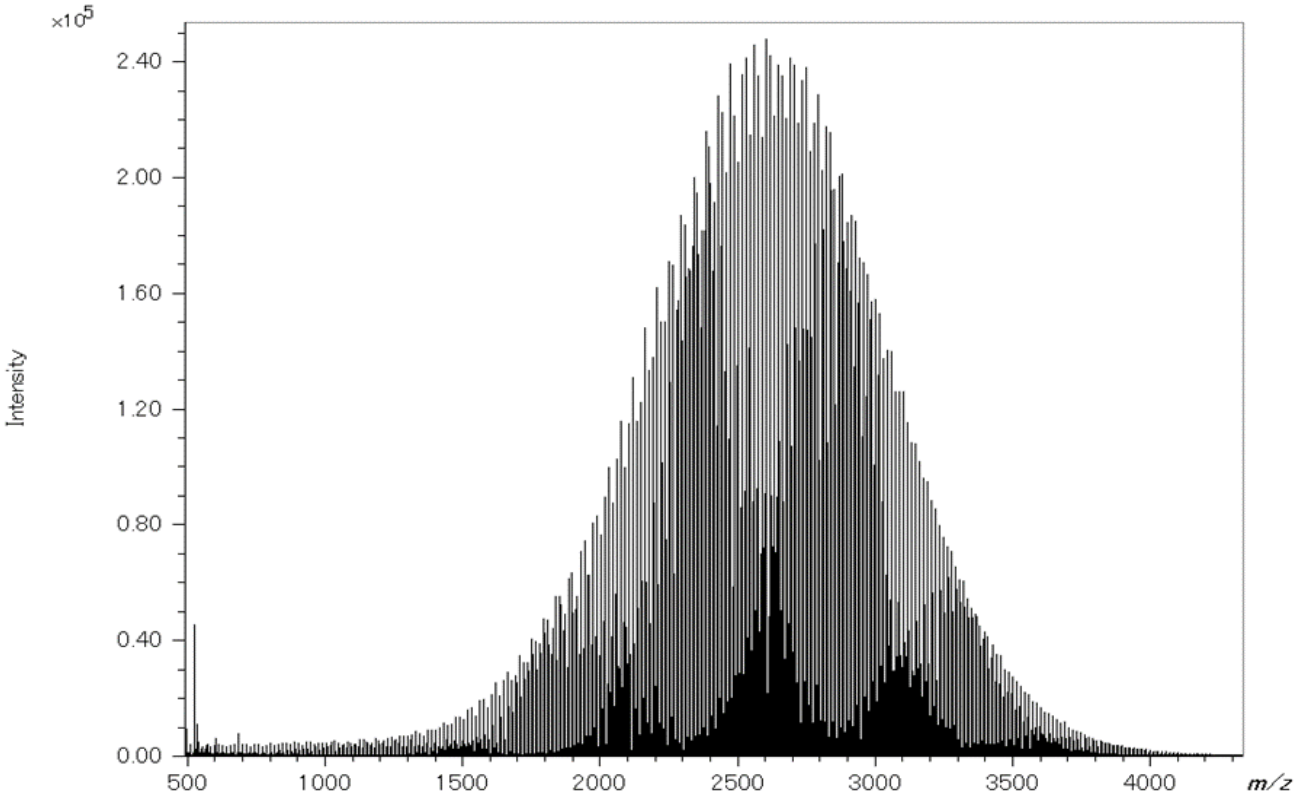
Poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol)



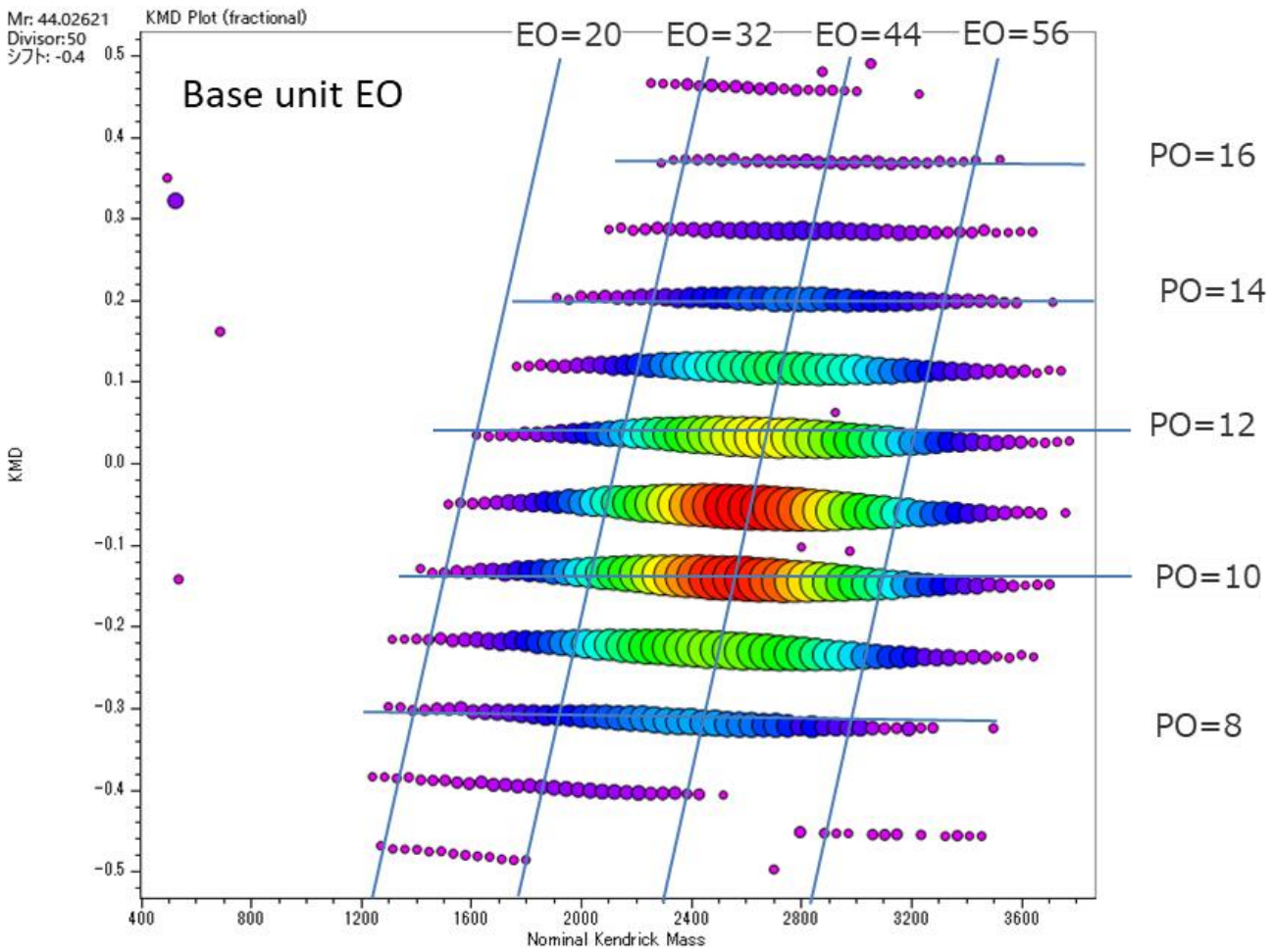
Structure	$O[O(CH_2)_2]_x$-*b*-$[OCH(CH_3)CH_2]_y$-*b*-$[O(CH_2)_2]_zOH$; $H(C_2H_4O)_{x+z}(C_3H_6O)_yOH$; PEG, 10 wt. %
Ion Species	$[M+Na]^+$
Molecular weight Information	M_n 1,101; M_w 1,128; D 1.025
Matrix	DCTB
Cationization agent	NaTFA
Mode	SpiralTOF:Positive ion



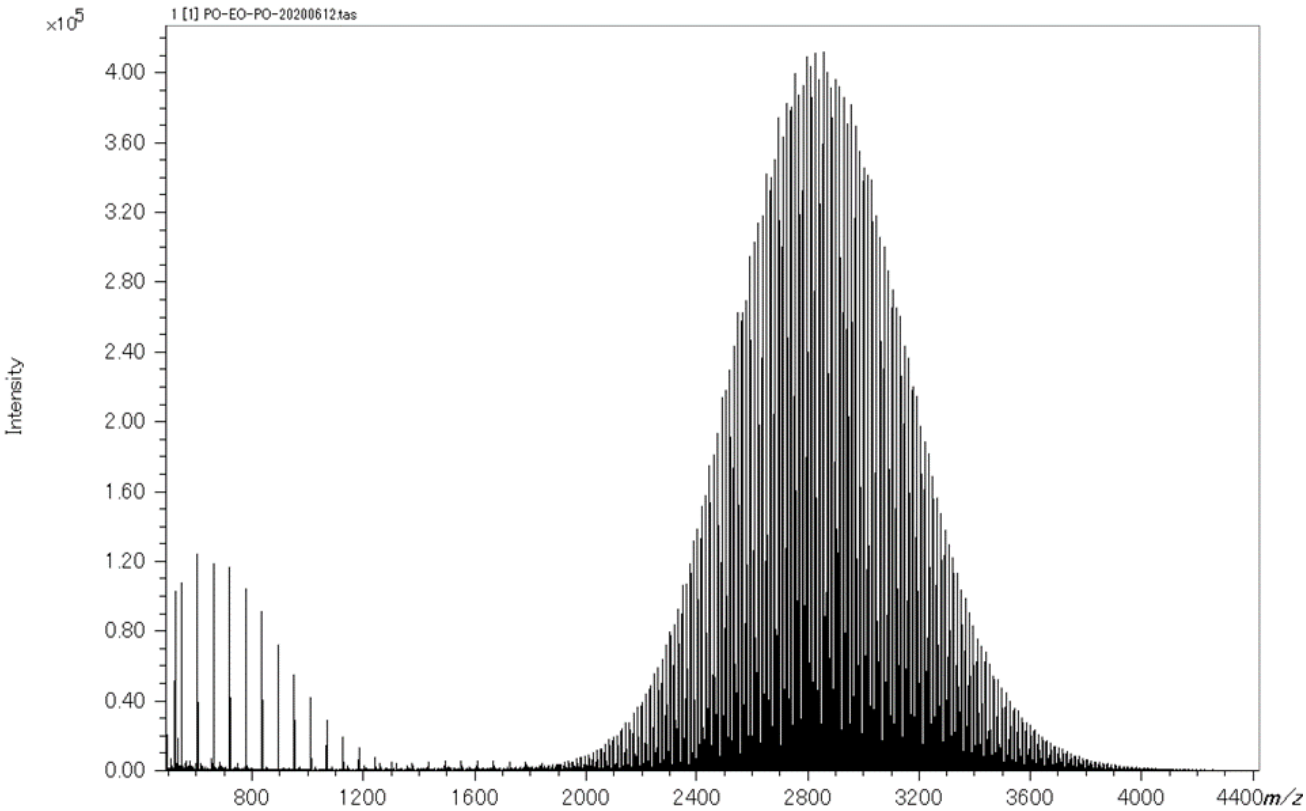
Poly(ethylene glycol-*ran*-propylene glycol)



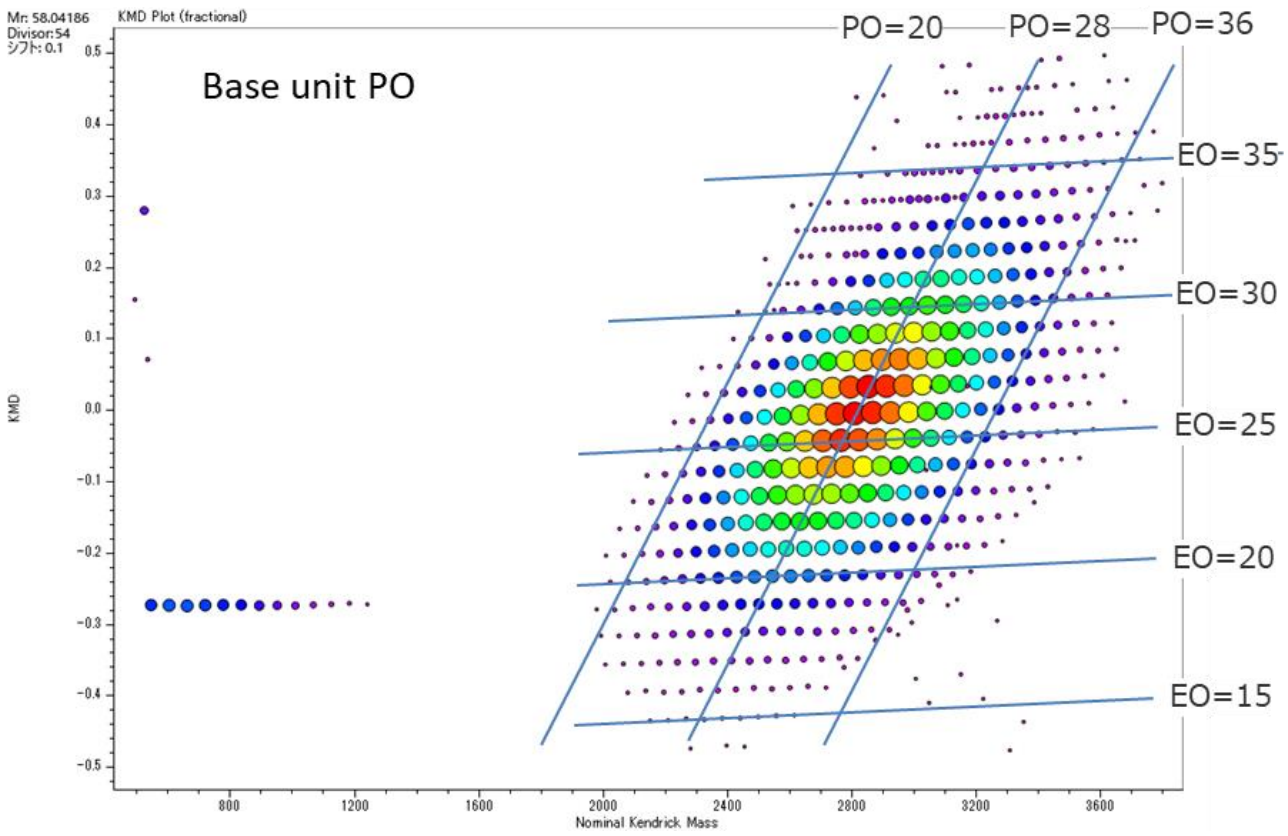
Structure	$H[O(CH_2)_2]_x$-*ran*-$[OCH(CH_3)CH_2]_yOH$; $O(C_2H_4O)_x(C_3H_6O)_yOH$
Ion Species	$[M+Na]^+$
Molecular weight Information	M_n 2,554; M_w 2,674; D 1.047
Matrix	DCTB
Cationization agent	NaTFA
Mode	SpiralTOF:Positive ion



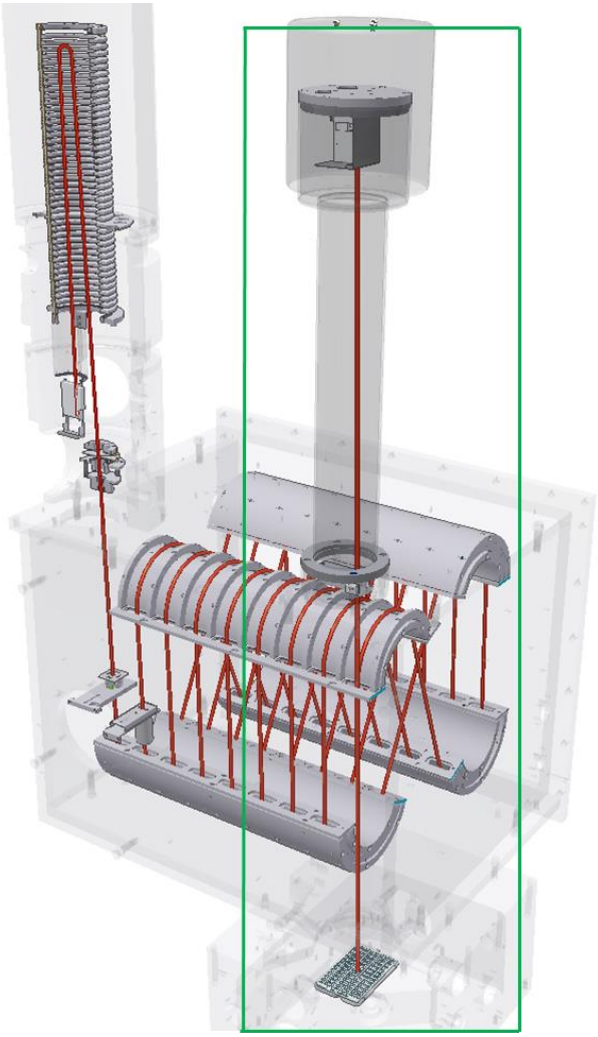
Poly(propylene glycol)-*block*-poly(ethylene glycol)-*block*-poly(propylene glycol)



Structure	$O[OCH(CH_3)CH_2]_x$-*b*-$[O(CH_2)_2]_y$-*b*-$[OCH(CH_3)CH_2]_zOH$; $H(C_3H_6O)_{x+z}(C_2H_4O)_yOH$; PEG, 40 wt. %
Ion Species	$[M+Na]^+$
Molecular weight Information	M_n 2,554; M_w 2,674; D 1.047
Matrix	DCTB
Cationization agent	NaTFA
Mode	SpiralTOF:Positive ion

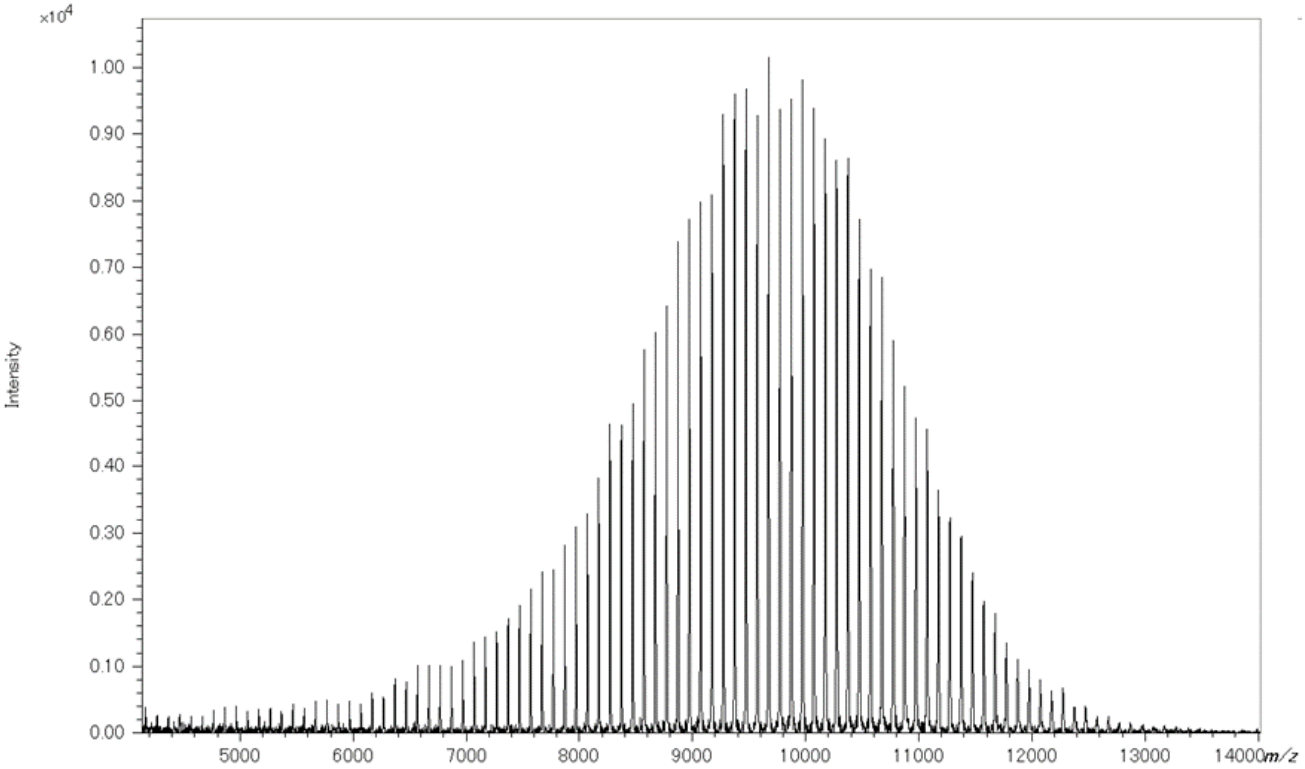


Linear Mode



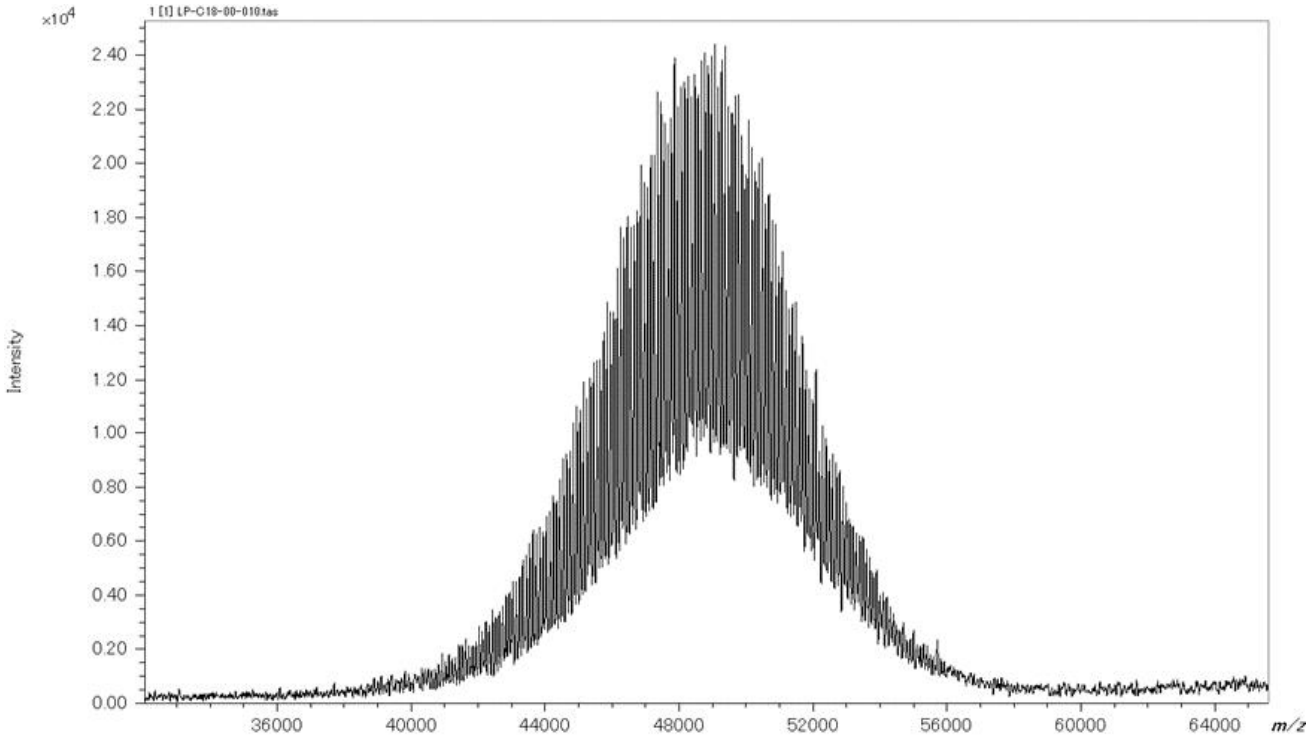
- Ions fly straight to the detector after being accelerated.
- High sensitivity can be achieved for high mass samples – suitable for polymers with the molecular weight of tens of thousands.
- The mass spectrum reflects ion population right after being accelerated – suitable for the determination of molecular weight distribution and for polymers that are easily fragmented.

PMMA (poly(methyl methacrylate)) MW 10 kDa



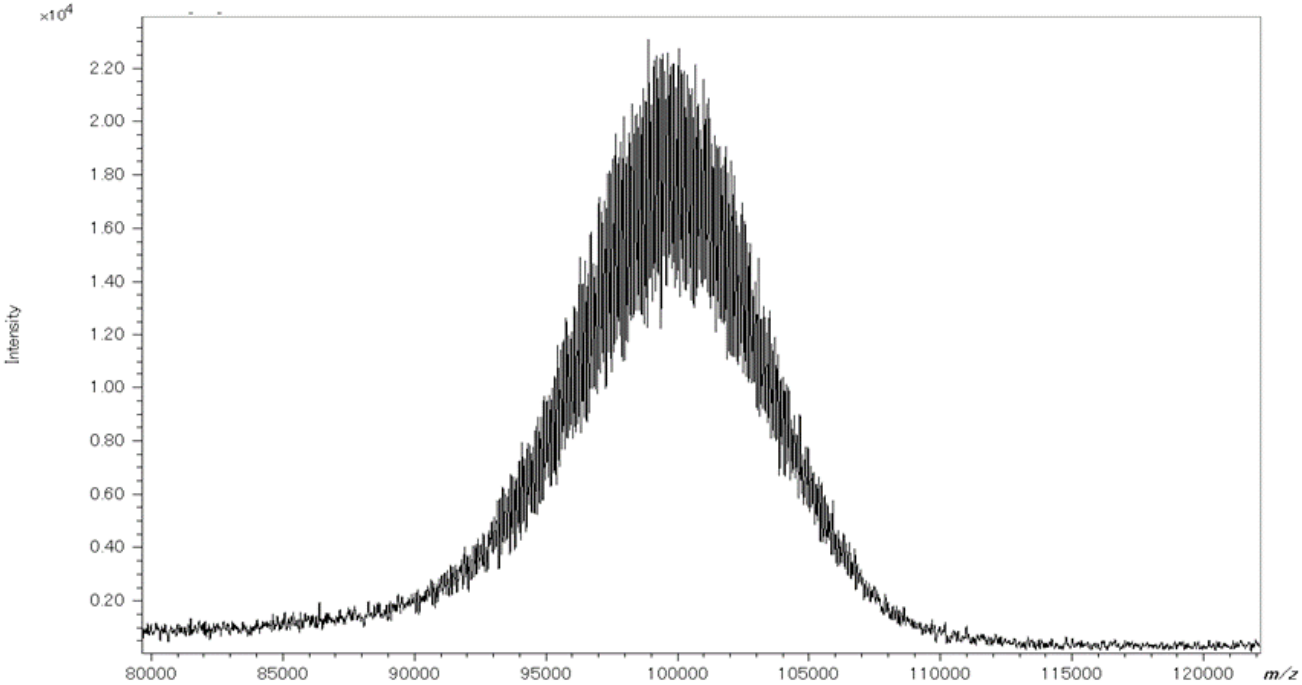
Structure	$H[CH_2C(CH_3)(CO_2CH_3)]_nH$; $H(C_5H_8O)_nH$
Ion Species	$[M+Na]^+$
Molecular weight Information	M_n 9,510; M_w 9,779; D 1.028
Matrix	DCTB
Cationization agent	NaTFA
Mode	Linear :Positive ion

PMMA (poly(methyl methacrylate)) MW 50 kDa



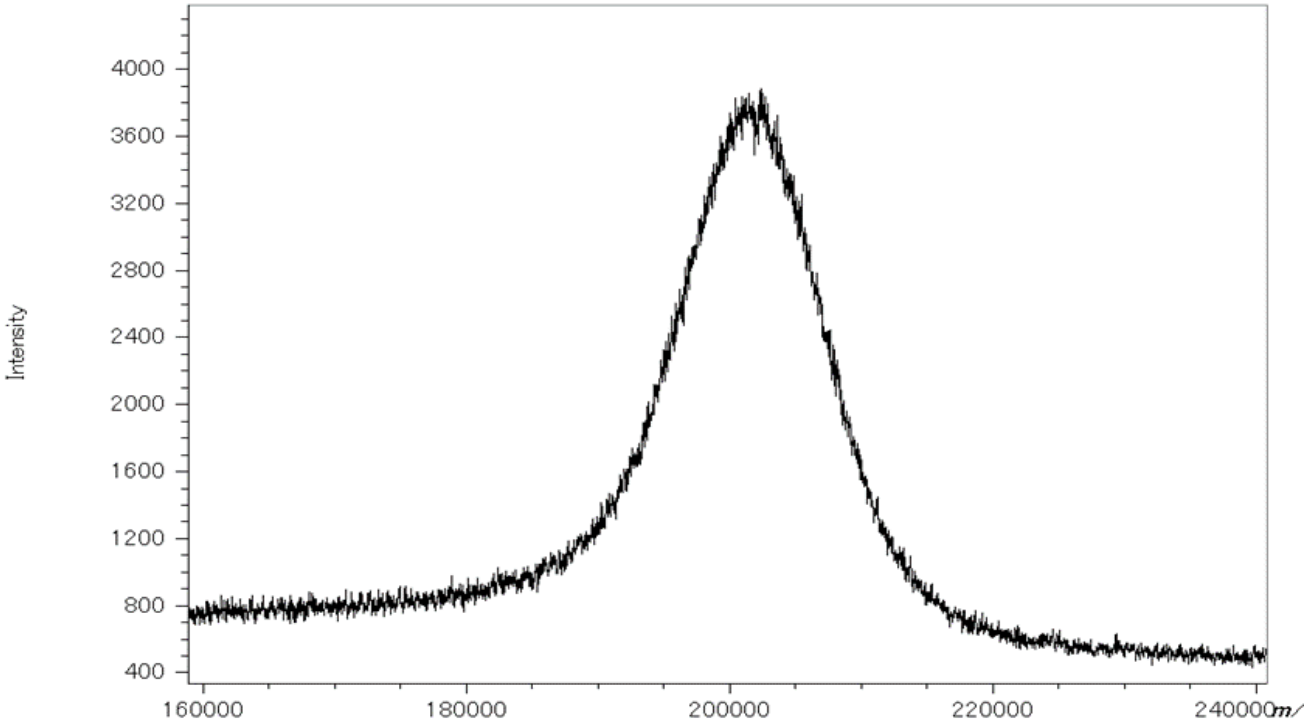
Structure	$H[CH_2C(CH_3)(CO_2CH_3)]_nH$; $H(C_5H_8O)_nH$
Ion Species	$[M+Na]^+$
Molecular weight Information	M_n 48,550; M_w 48,821; D 1.006
Matrix	DCTB
Cationization agent	NaTFA
Mode	Linear :Positive ion

PS (poly(styrene)) MW 100 kDa



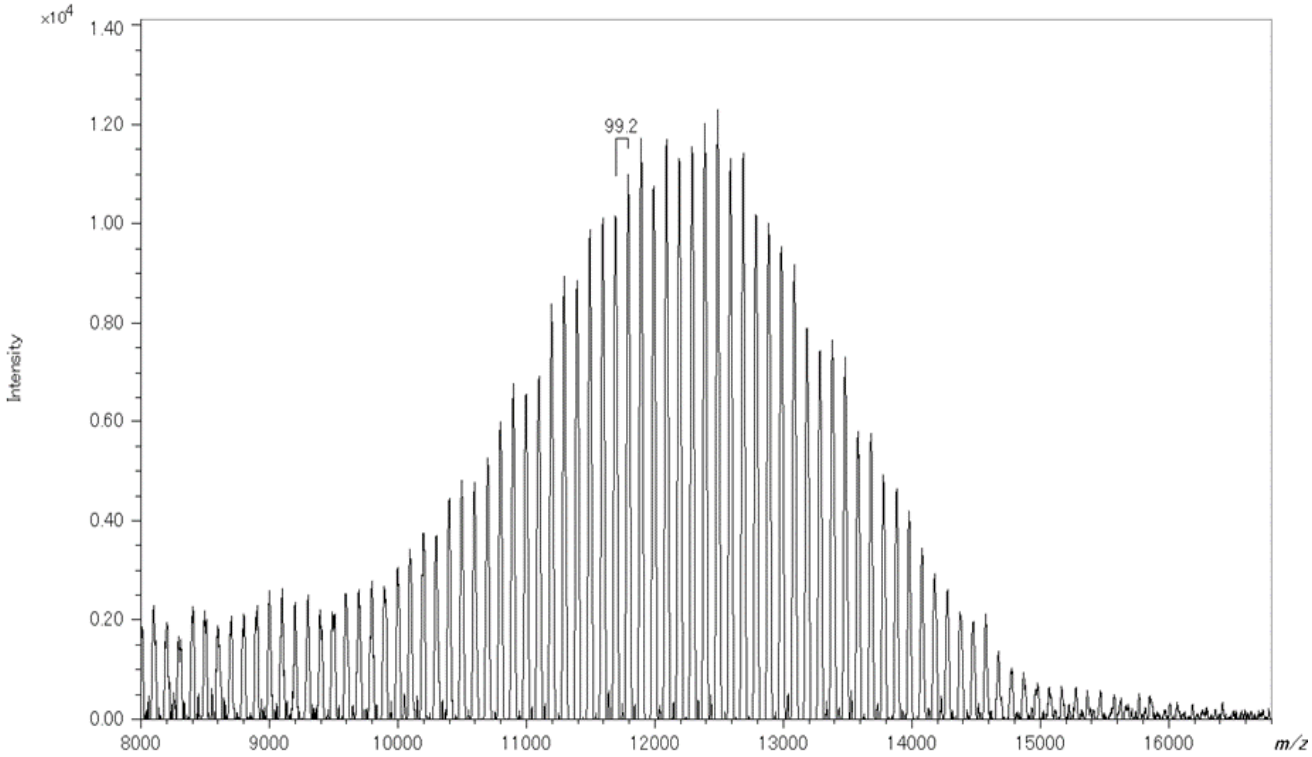
Structure	$-(C_8H_8)-$
Ion Species	$[M+Ag]^+$
Molecular weight Information	M_n 97,059; M_w 97,861; D 1.008
Matrix	DCTB
Cationization agent	AgTFA
Mode	Linear :Positive ion

PS (poly(styrene)) MW 200 kDa



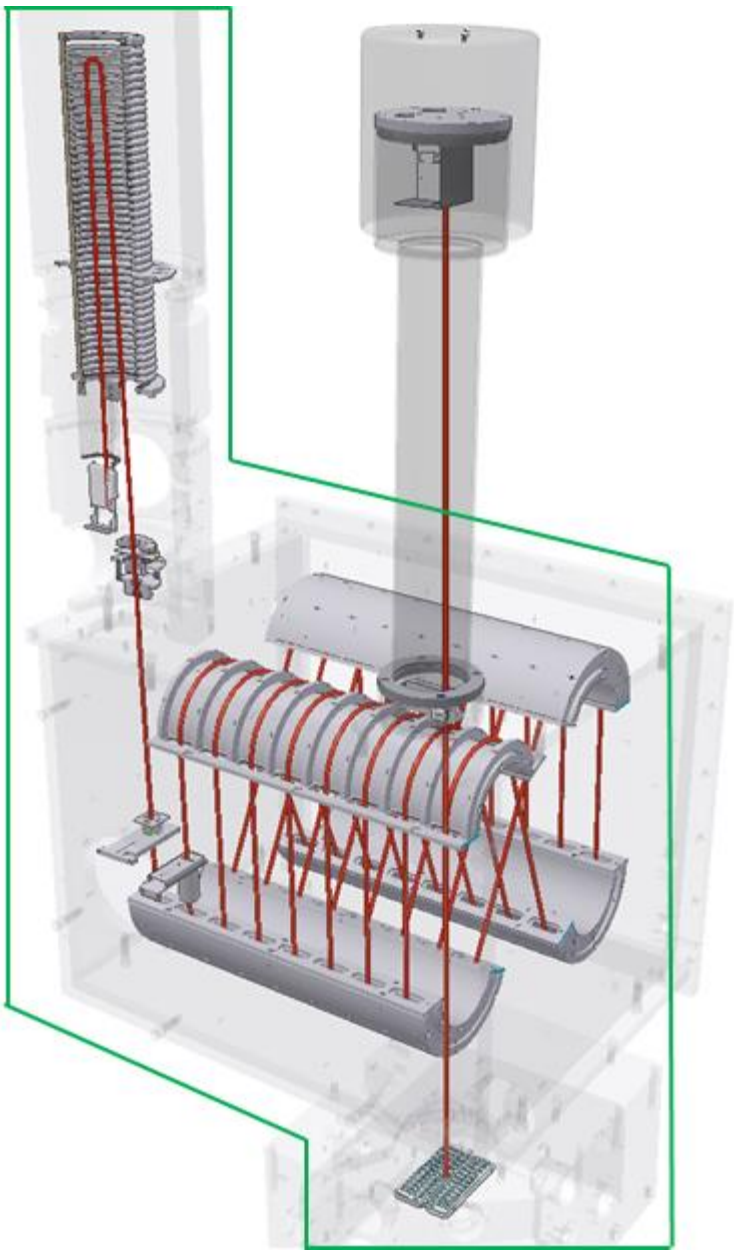
Structure	$-[CH_2CH(C_6H_5)]_n-$; $-(C_8H_8)_n-$
Ion Species	$[M+Ag]^+$
Molecular weight Information	M_n 197,860; M_w 199,401; D 1.008
Matrix	DCTB
Cationization agent	AgTFA
Mode	Linear :Positive ion

POZ (poly(2-ethyl-2-oxazoline)) MW 10 kDa



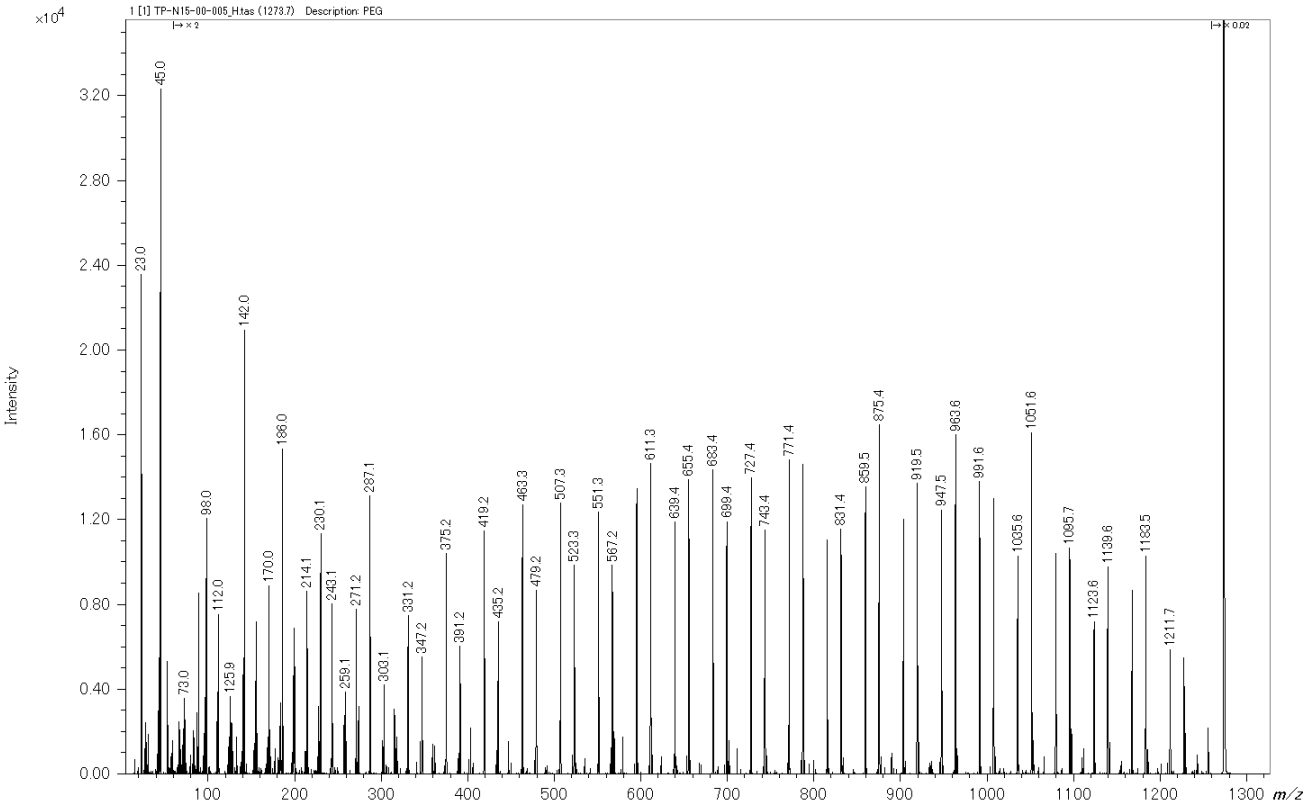
Structure	$CH_3[N(COC_2H_5)CH_2CH_2]_nOH$; $CH_3(C_5H_9NO)OH$
Ion Species	$[M+Na]^+$
Molecular weight Information	M_n 11,307; M_w 11,,596; D 1.026
Matrix	DCTB
Cationization agent	NaTFA
Mode	Linear :Positive ion

TOF-TOF Mode



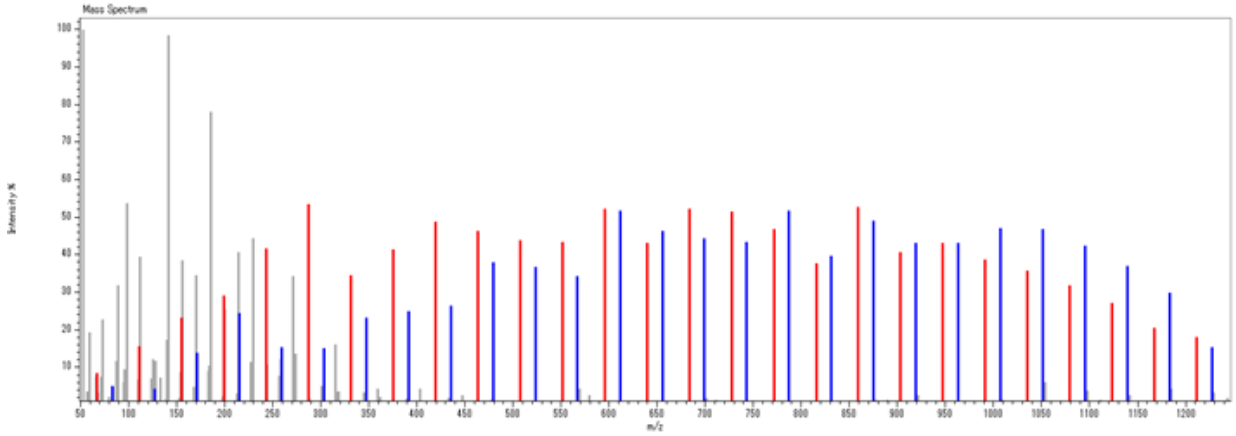
- Information-rich product ion spectra with high-energy collision induced dissociation (HE-CID).
- High precursor ion selectivity due to long flight distance of 15 m from the ion source to the ion gate.
- The Offset Parabolic Reflectron used in the 2nd TOFMS can detect product ions over a wide mass range from alkali metal adduct ions to the precursor ions.

PEO (poly(ethylene oxide))

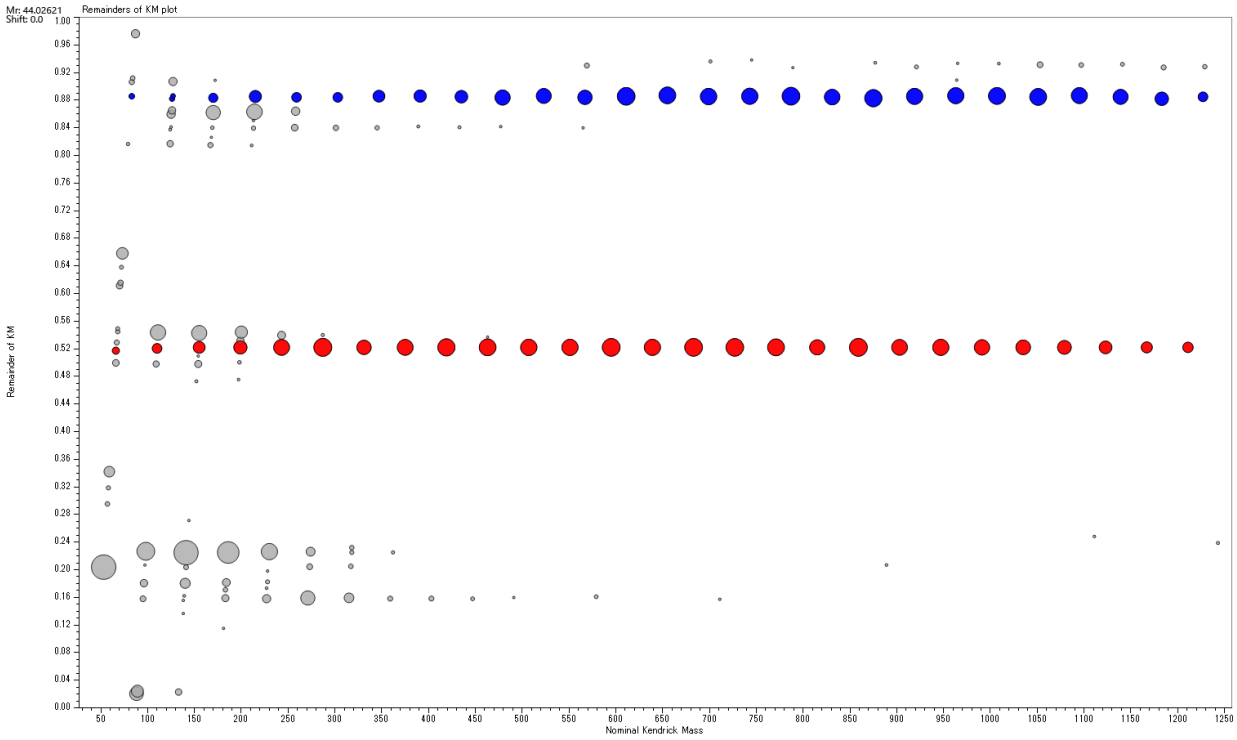


Structure	$HO(CH_2CH_2O)_nH$
Ion Species	$[M+Na]^+$
Precursor ion	*m/z* 1,273.73380 (n = 28)
Matrix	DCTB
Cationization agent	NaTFA
Mode	TOF-TOF :Positive ion

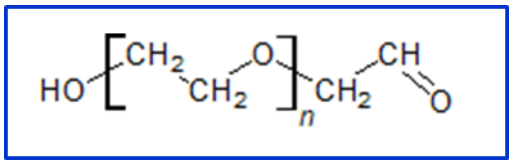
Peak list

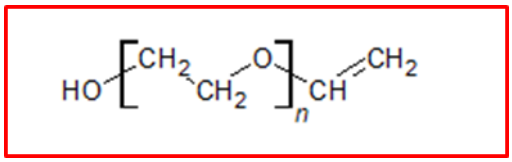


RKM Plot

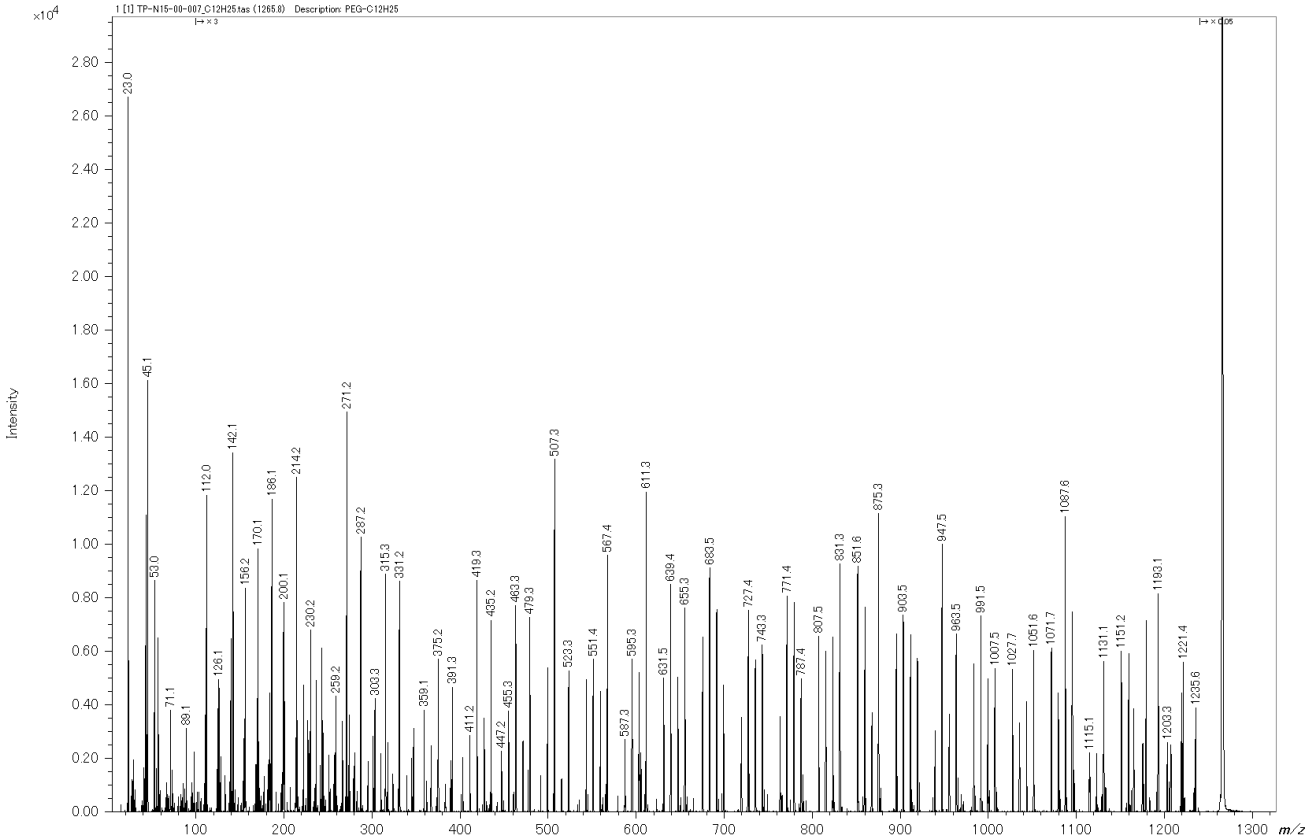


Estimated Structure



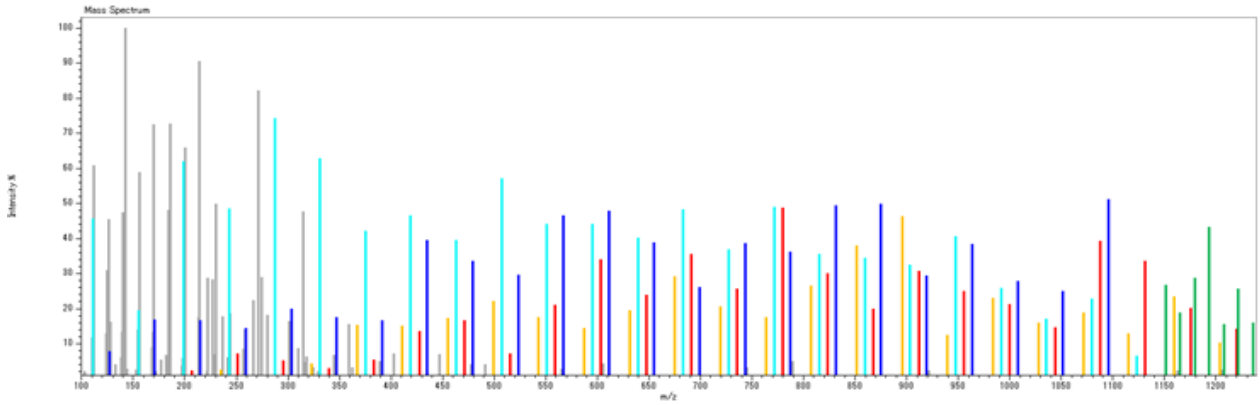


Polyethylene glycol monododecyl ether

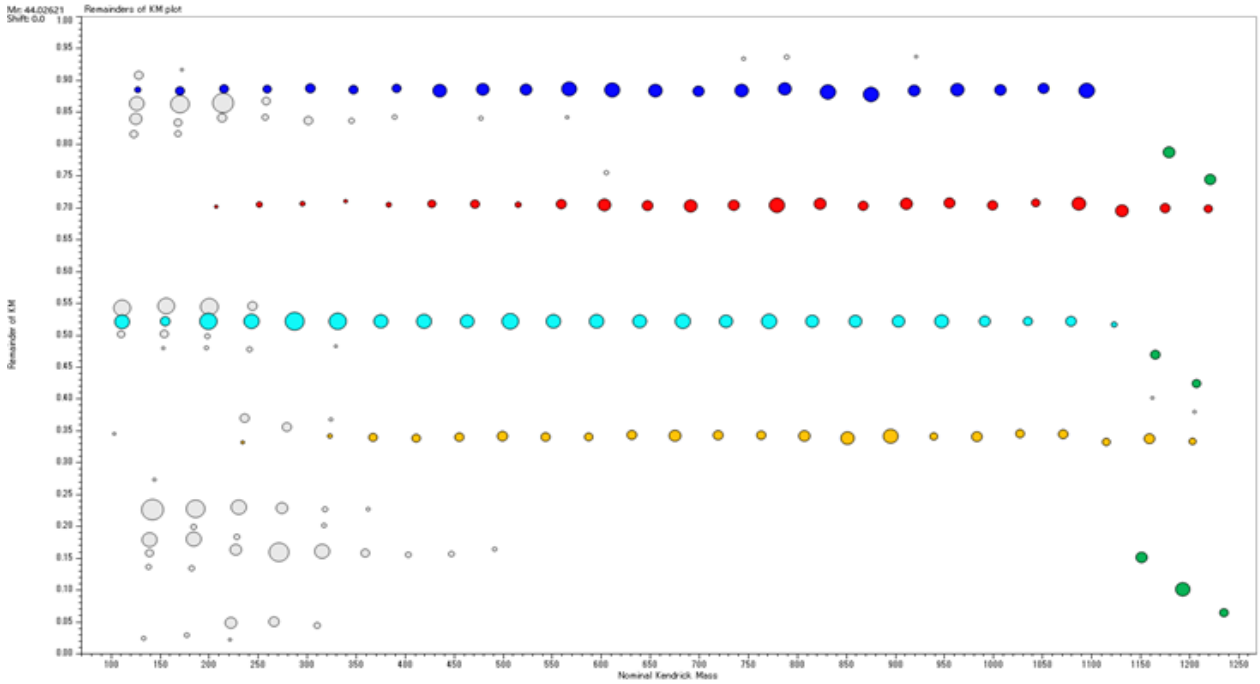


Structure	$HO[(CH_2)_2O]_n(CH_2)_{11}CH_3$; $HO(C_2H_4O)_nC_{12}H_{25}$
Ion Species	$[M+Na]^+$
Precursor ion	*m/z* 1,265.817 (n = 24)
Matrix	DCTB
Cationization agent	NaTFA
Mode	TOF-TOF:Positive ion

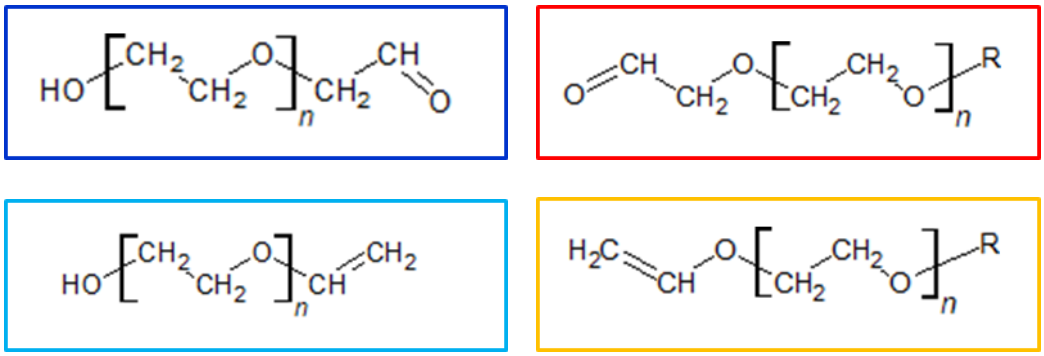
Peak list



RKM Plot



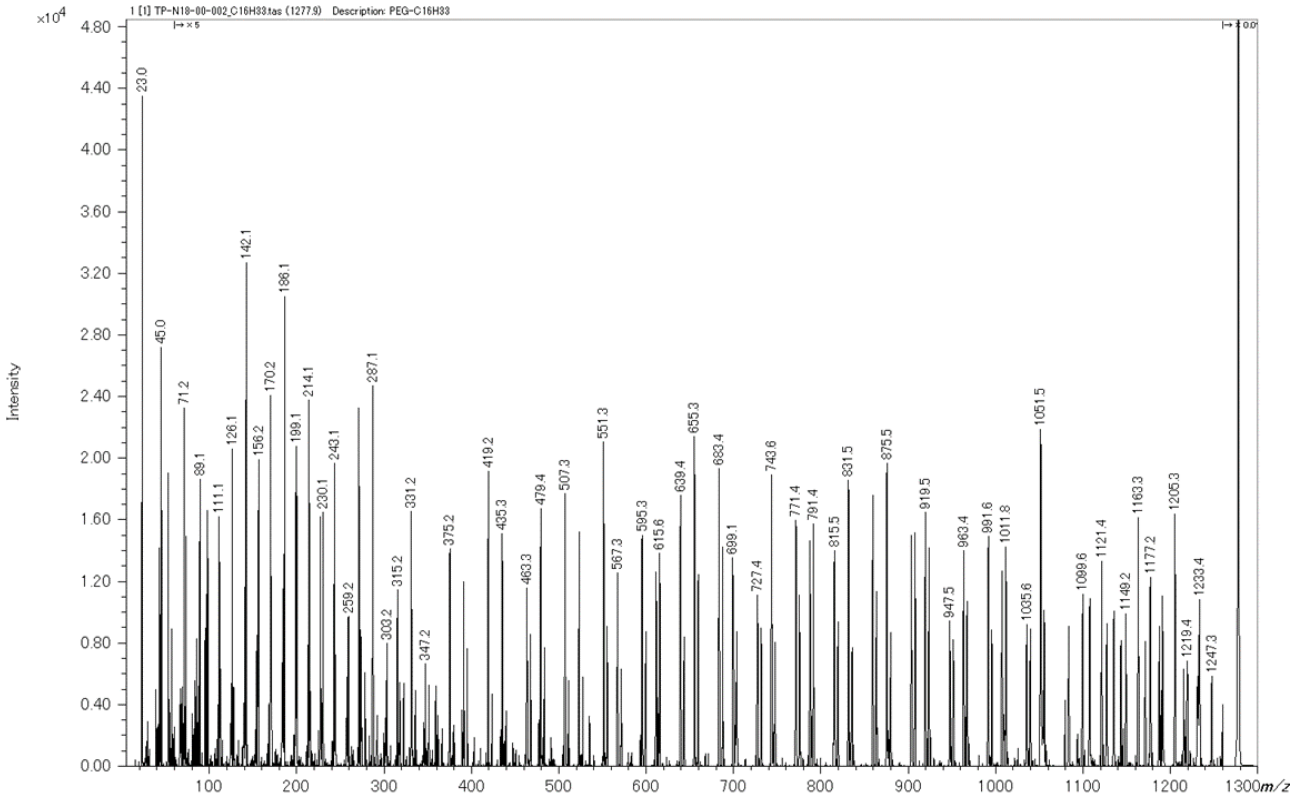
Estimated Structure



Alkyl group (R) fragment

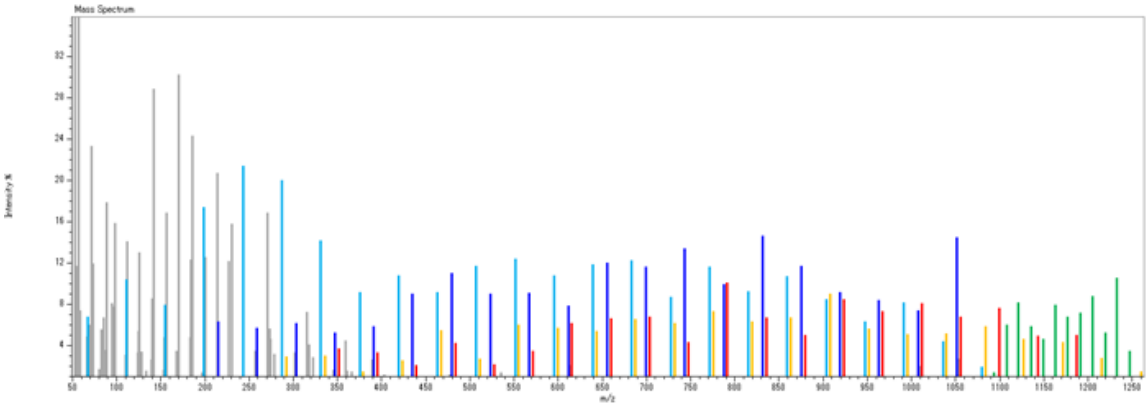
R = $C_{12}H_{25}$

Polyethylene glycol monocetyl ether

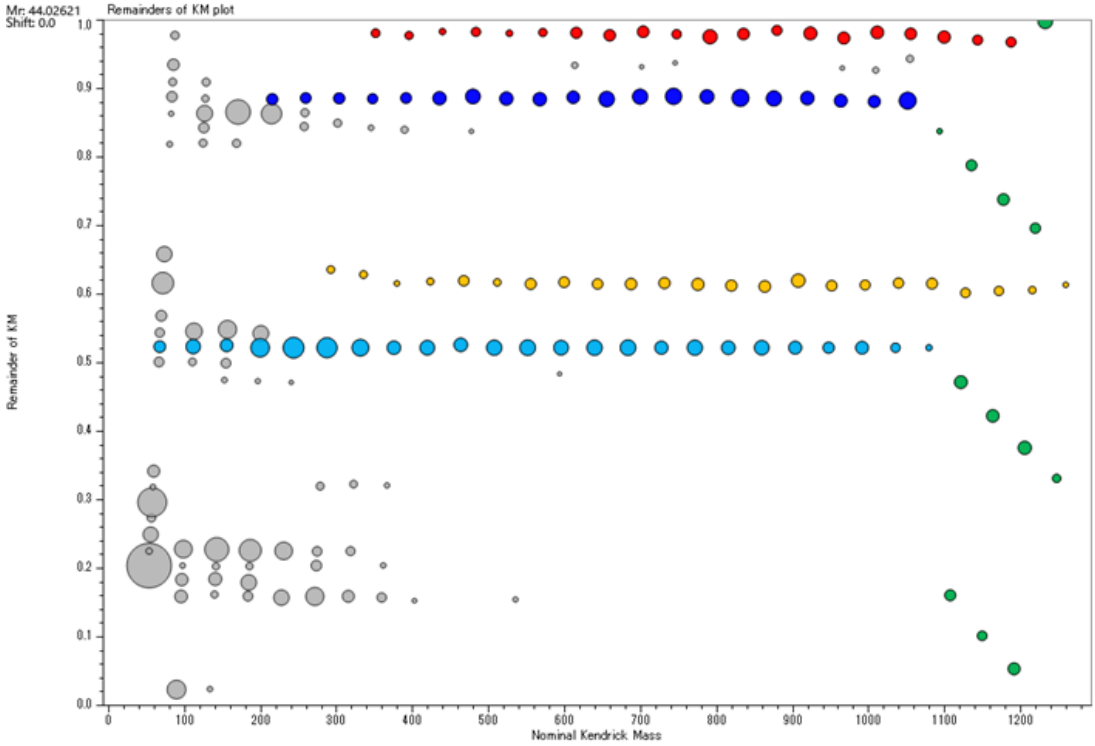


Structure	$HO[(CH_2)_2O]_n(CH_2)_{15}CH_3$; $HO(C_2H_4O)_nC_{16}H_{33}$
Ion Species	$[M+Na]^+$
Precursor ion	*m/z* 1,277.853 (n = 23)
Matrix	DCTB
Cationization agent	NaTFA
Mode	TOF-TOF:Positive ion

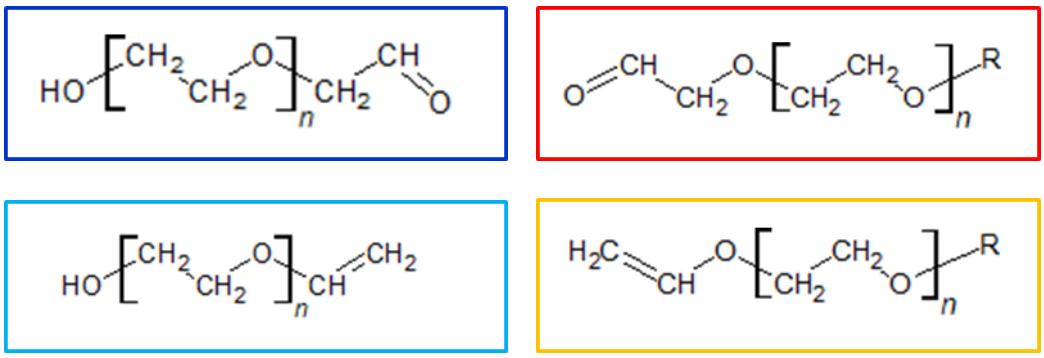
Peak list



RKM Plot



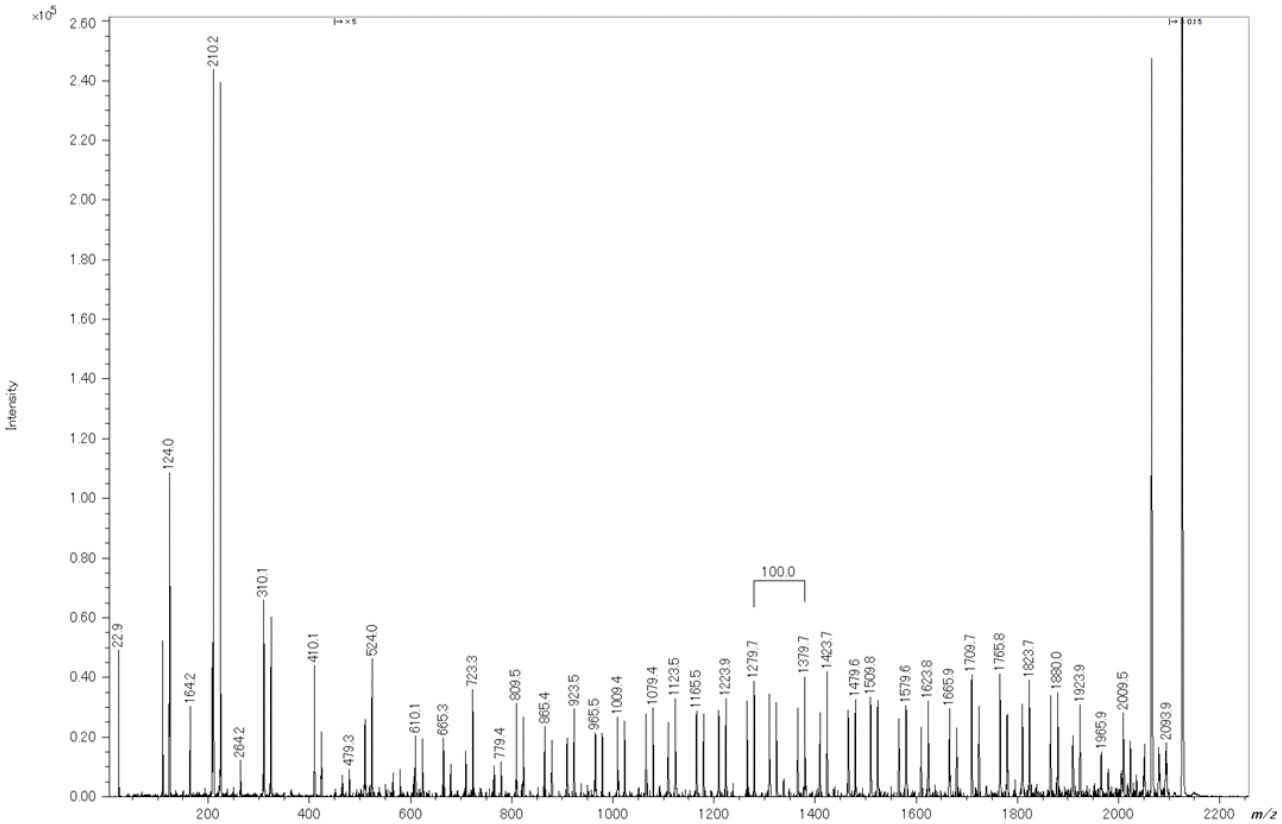
Estimated Structure



Alkyl group (R) fragment

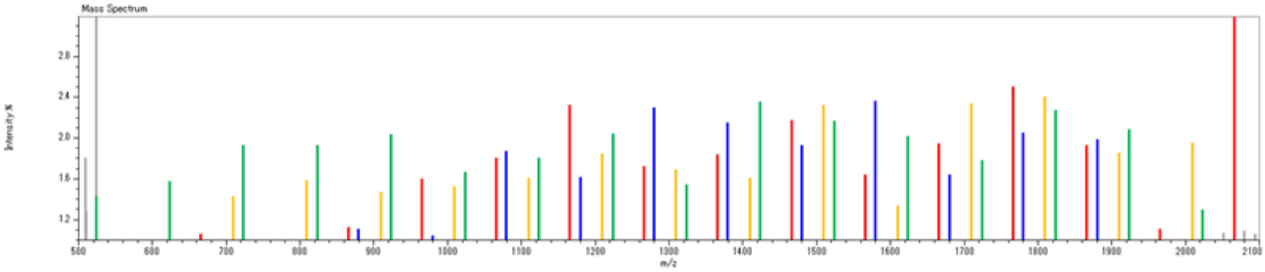
R = $C_{12}H_{25}$

PMMA (poly(methyl methacrylate))

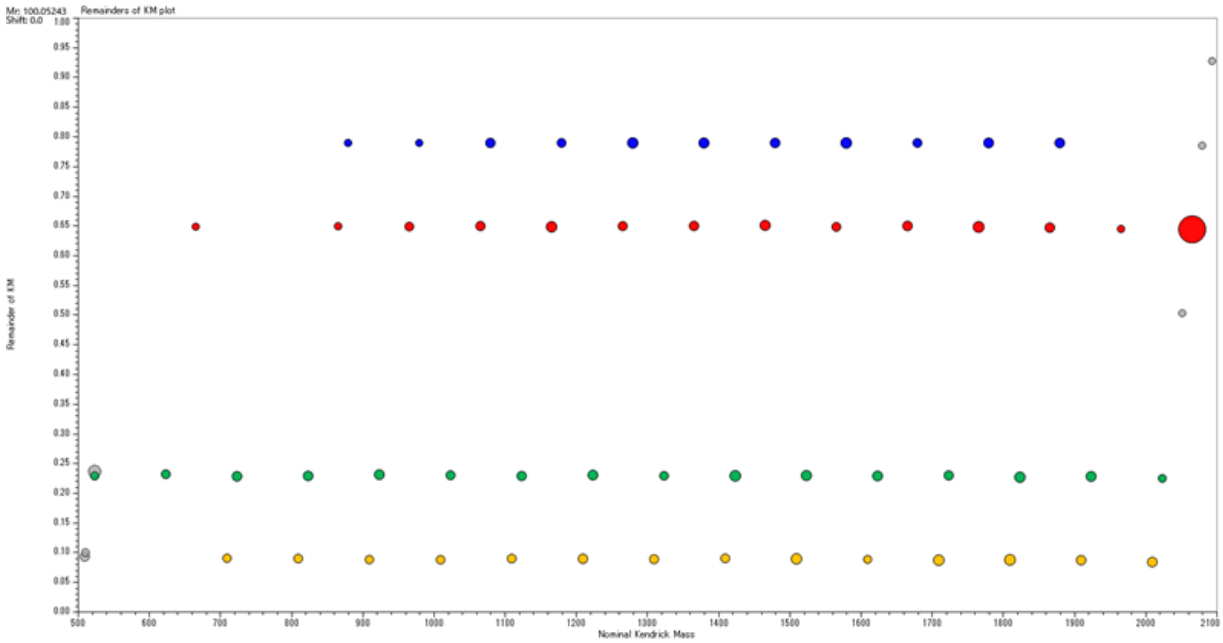


Structure	$HO(CH_2CH_2O)_nH$; $HO(C_2H_4O)_nH$
Ion Species	$[M+Na]^+$
Precursor ion	*m/z* 2,125 (n = 25)
Matrix	DCTB
Cationization agent	NaTFA
Mode	TOF-TOF:Positive ion

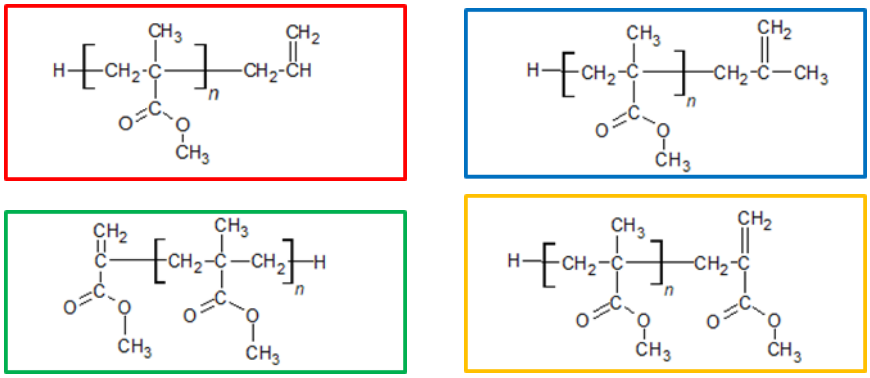
Peak list



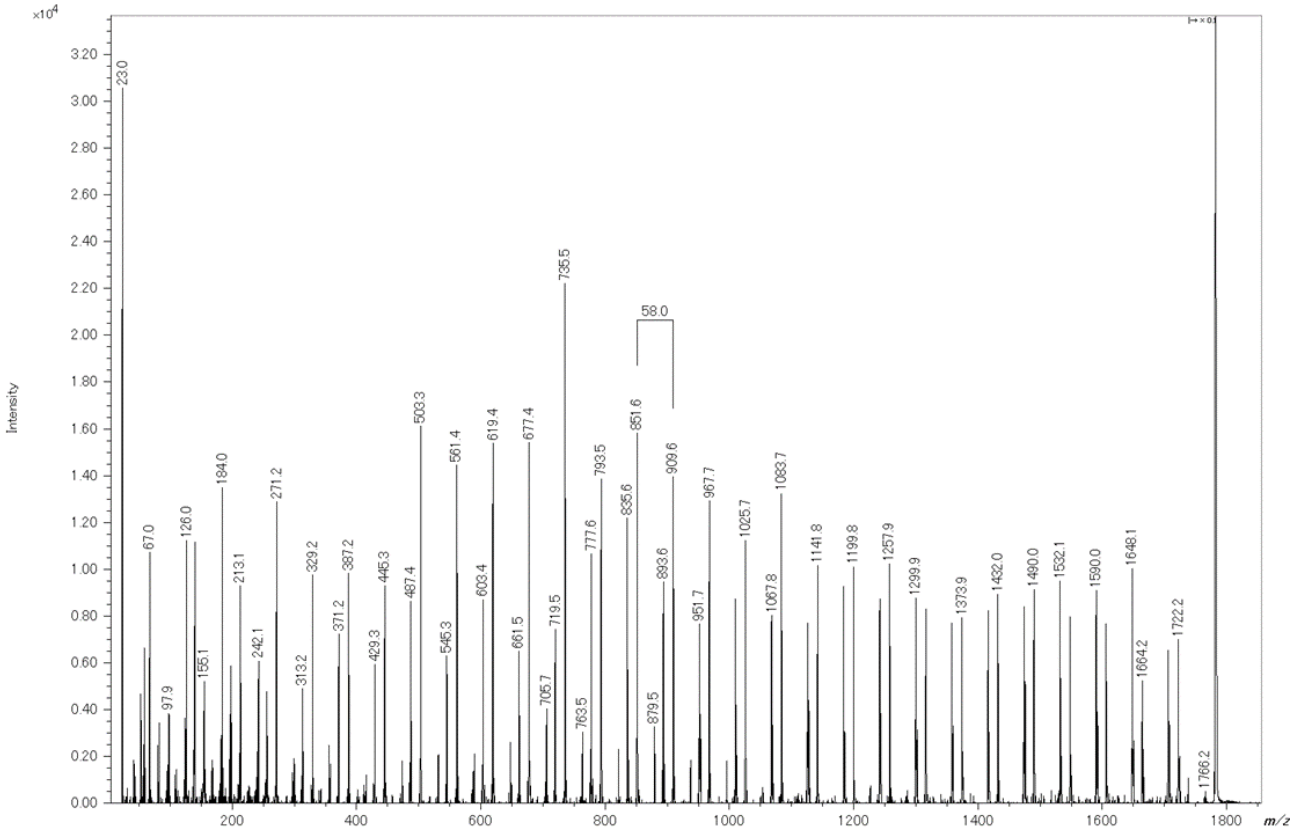
RKM Plot



Estimated Structure

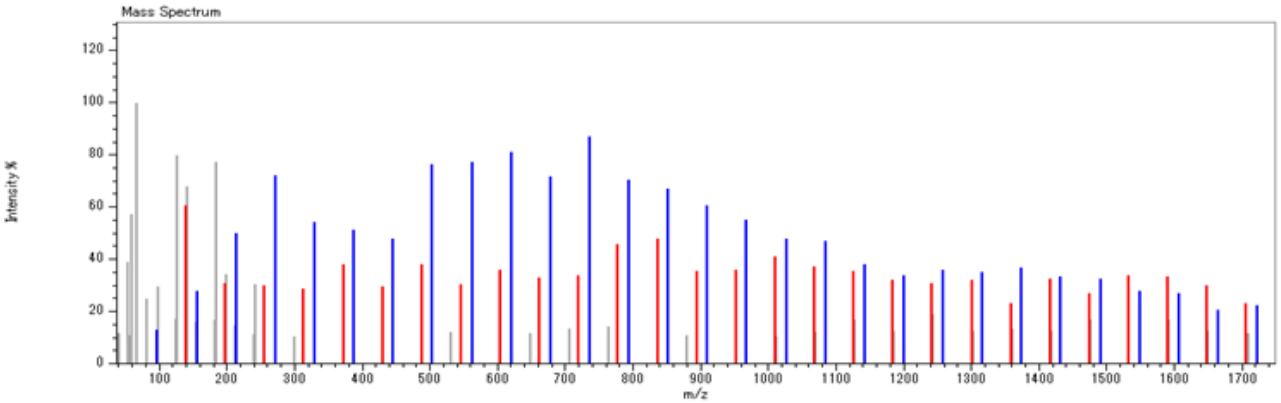


PPO (poly(propylene oxide))

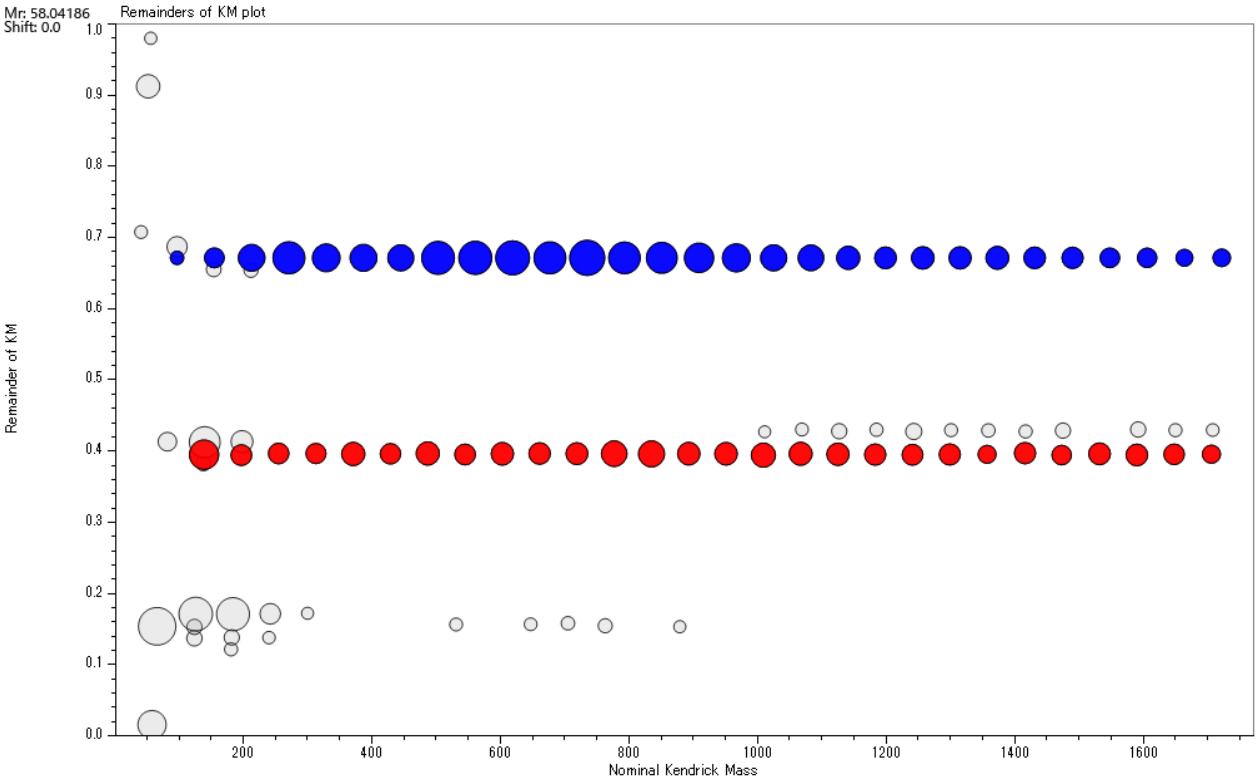


Structure	$HO[CH_2CH(CH_3)O]_nH$; $HO(C_3H_6O)_nH$
Ion Species	$[M+Na]^+$
Precursor ion	*m/z* 1,782.25573 (n = 30)
Matrix	DCTB
Cationization agent	NaTFA
Mode	TOF-TOF:Positive ion

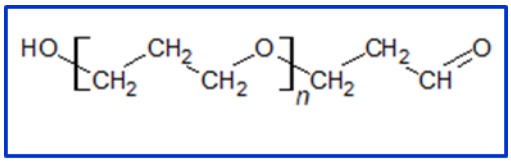
Peak list

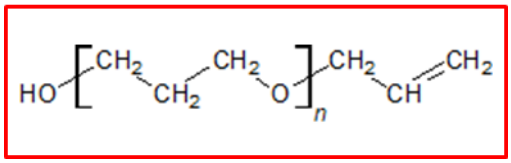


RKM Plot

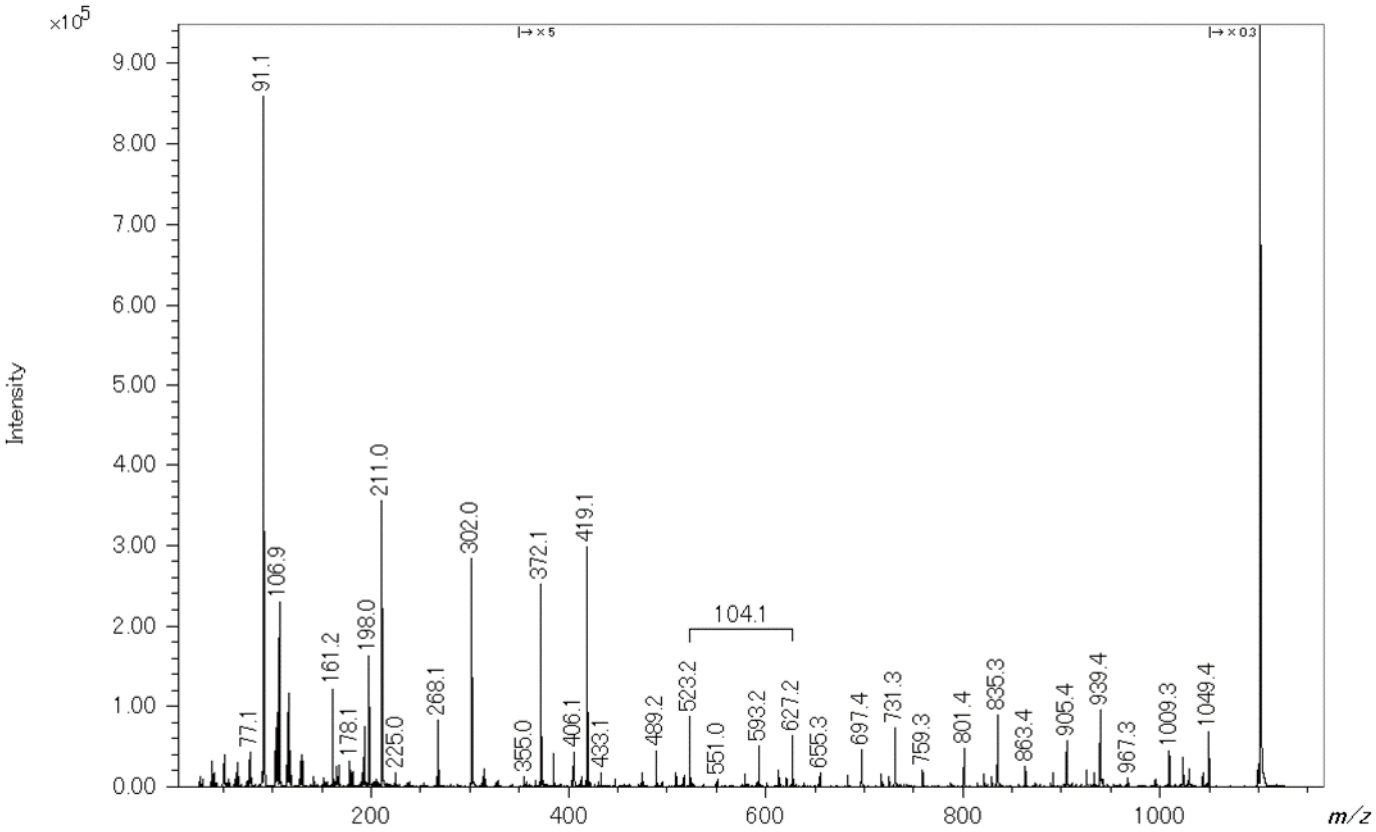


Estimated Structure



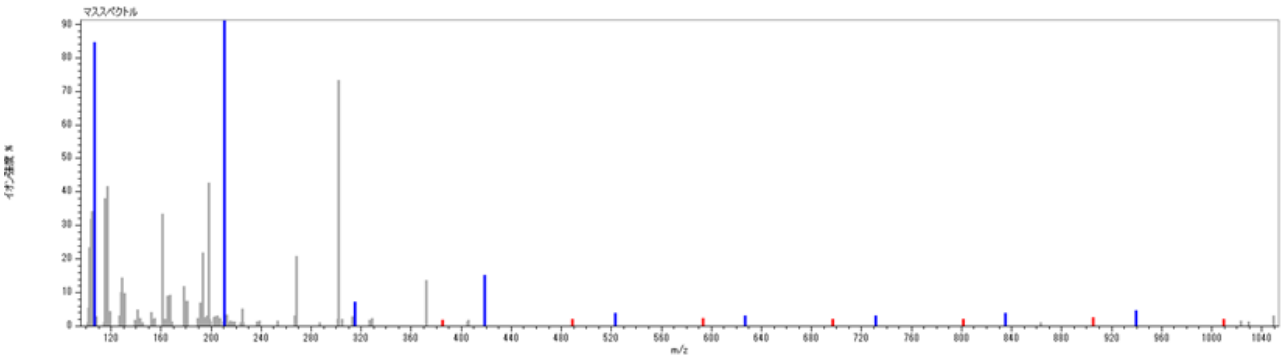


PS (poly(styrene))

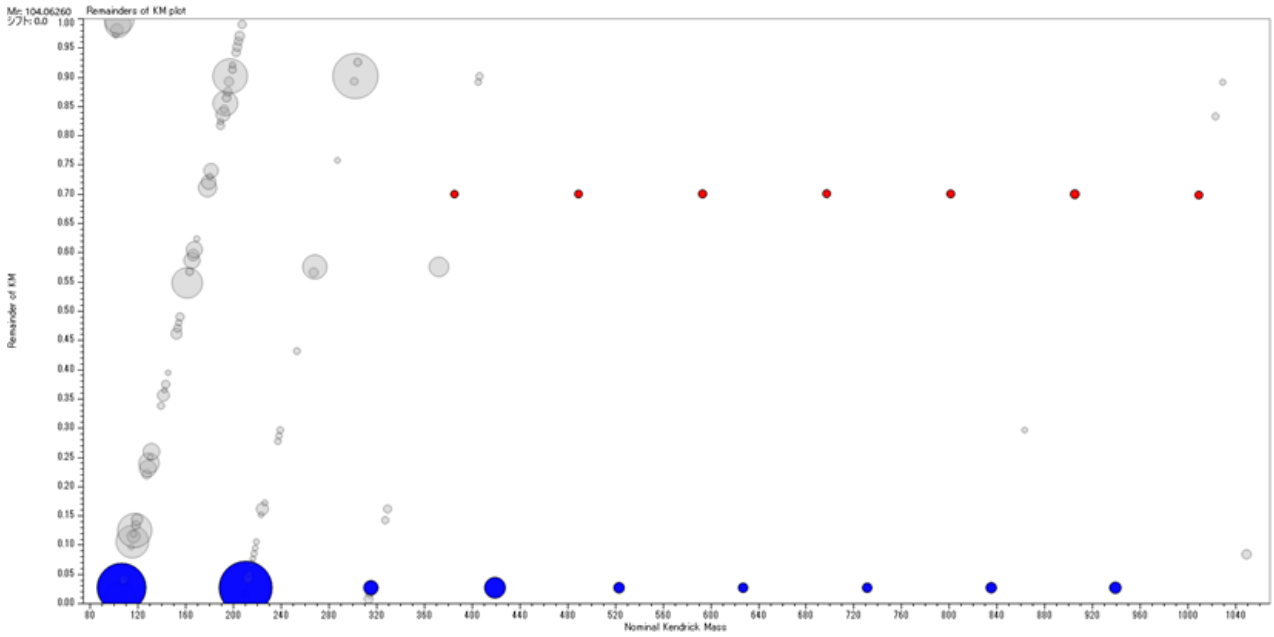


Structure	$H[CH_2CH(C_6H_5)]_nC4H9$; $H(C_8H_8)_nC_4H_9$
Ion Species	$[M+Na]^+$
Precursor ion	*m/z* 1,101.5462 (n = 9)
Matrix	DCTB
Cationization agent	AgTFA
Mode	TOF-TOF:Positive ion

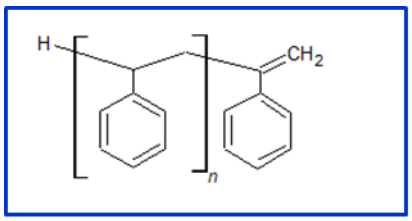
Peak list

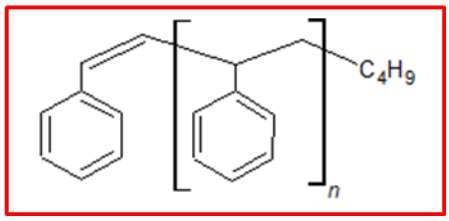


RKM Plot

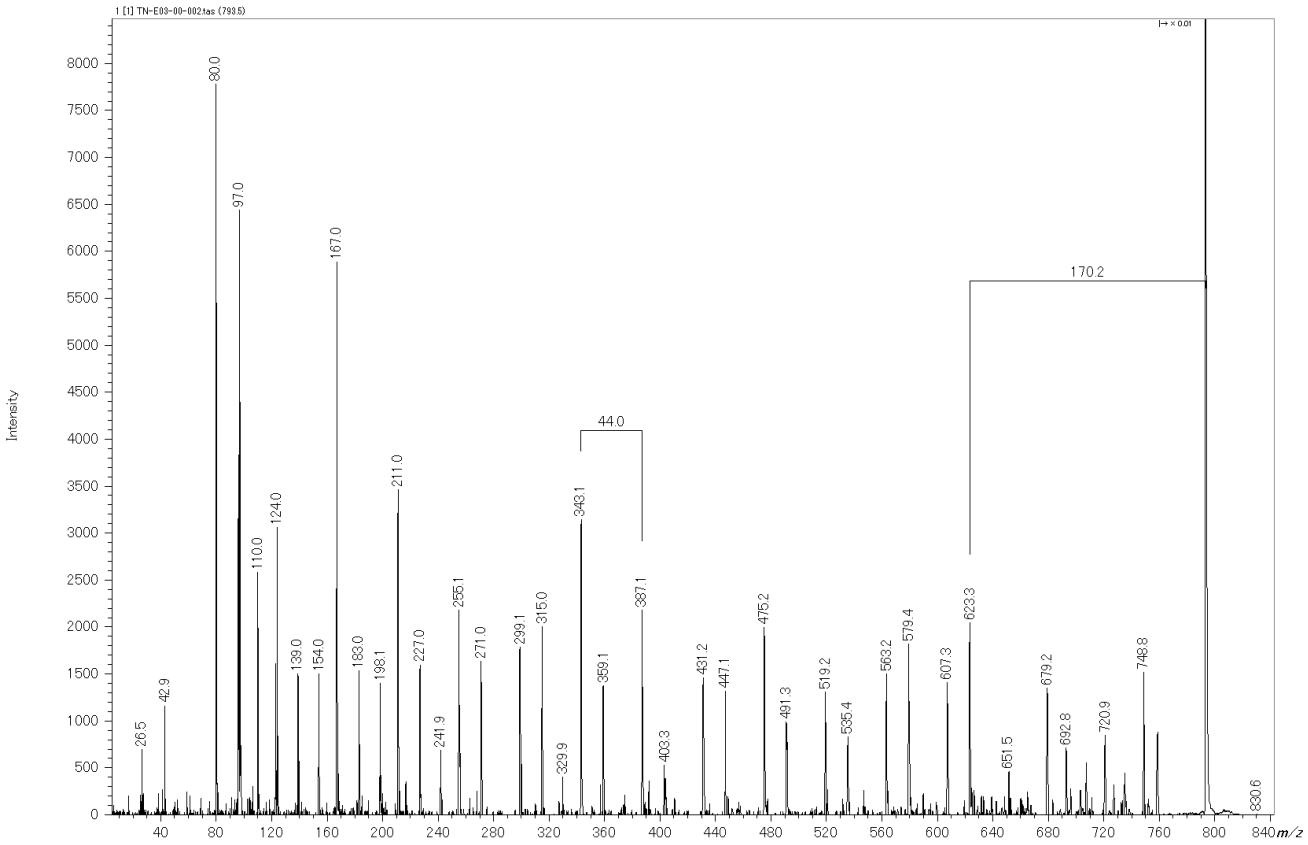


Estimated Structure

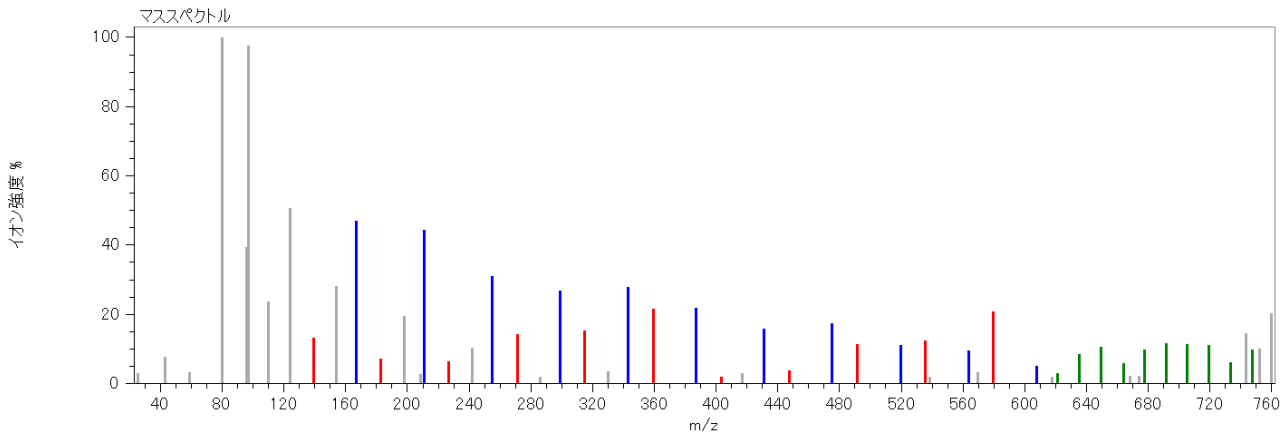


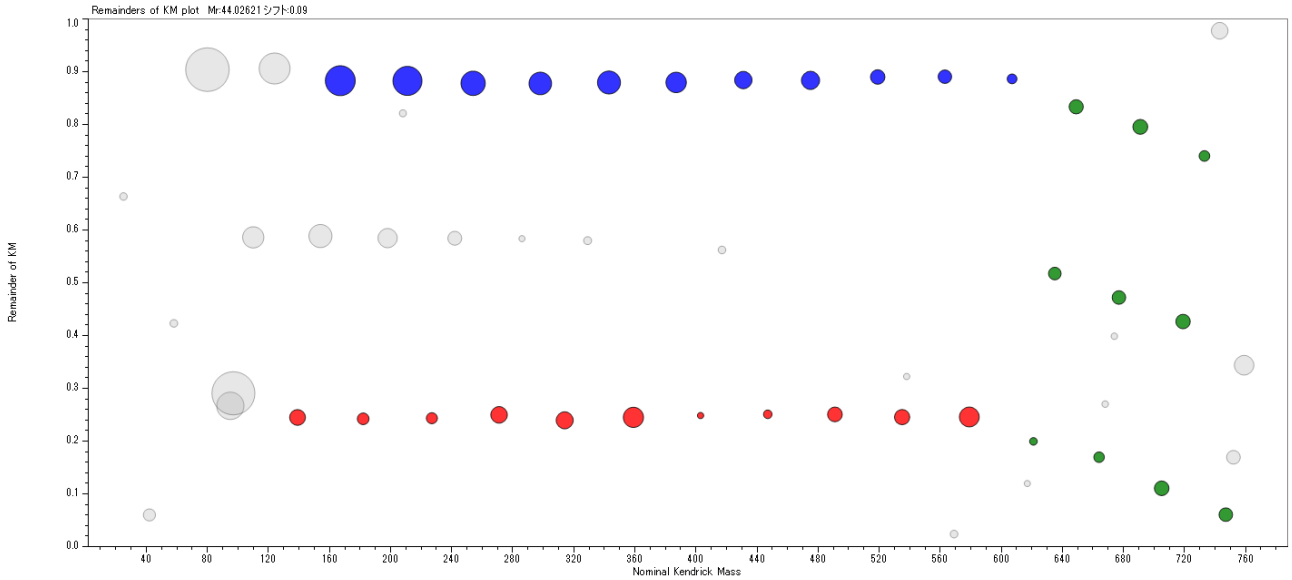


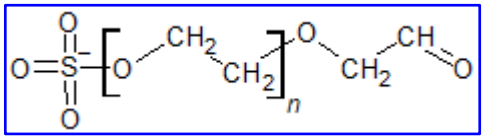
Polyoxyethylene alkyl ether sulfuric acid

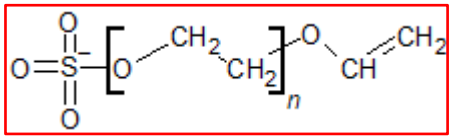


Structure	$NaSO_3[(CH_2)_2O]_nO(CH_2)_{11}CH_3$; $NaSO_3(C_2H_4O)_nOC_{12}H_{25}$
Ion Species	$[M-Na]^-$
Precursor ion	*m/z* 793.46248 (n = 12)
Matrix	CHCA
Cationization agent	None
Mode	TOF-TOF:Negative ion









Alkyl group (R) fragment

Index

Certain products in this brochure are controlled under the "Foreign Exchange and Foreign Trade Law" of Japan in compliance with international security export control. JEOL Ltd. must provide the Japanese Government with "End-user's Statement of Assurance" and "End-use Certificate" in order to obtain the export license needed for export from Japan. If the product to be exported is in this category, the end user will be asked to fill in these certificate forms.

JEOL Ltd.

3-1-2 Musashino Akishima Tokyo 196-8558 Japan Sales Division Tel. +81-3-6262-3560 Fax. +81-3-6262-3577

www.jeol.com ISO 9001 • ISO 14001 Certified

• **AUSTRALIA & NEW ZEALAND** /JEOL (AUSTRALASIA) Pty.Ltd. Suite 1, L2 18 Aquatic Drive - Frenchs Forest NSW 2086 Australia • **BELGIUM** /JEOL (EUROPE) B.V. Planet II, Gebouw B Leuvensesteenweg 542, B-1930 Zaventem Belgium • **BRAZIL** /JEOL Brasil Instrumentos Cientificos Ltda. Av. Jabaquara, 2958 5° andar conjunto 52 ; 04046-500 Sao Paulo, SP Brazil • **CANADA** /JEOL CANADA, INC. 3275 1ere Rue, Local #8 St-Hubert, QC J3Y-8Y6, Canada • **CHINA** /JEOL (BEIJING) CO., LTD. Zhongkeziyuan Building South Tower 2F, Zhongguancun Nansanjie Street No. 6, Haidian District, Beijing, P.R.China • **EGYPT** /JEOL SERVICE BUREAU 3rd Fl. Nile Center Bldg., Nawal Street, Dokki, (Cairo), Egypt • **FRANCE** /JEOL (EUROPE) SAS Espace Claude Monet, 1 Allee de Giverny 78290, Croissy-sur-Seine, France • **GERMANY** /JEOL (GERMANY) GmbH Gute Aenger 30 85356 Freising, Germany • **GREAT BRITAIN & IRELAND** /JEOL (U.K.) LTD. Silver Court, Watchmead, Welwyn Garden City, Hertfordshire AL7 1LT, U.K. • **INDIA** /JEOL INDIA PVT. LTD. Unit No.305, 3rd Floor, ABW Elegance Tower, Jasola District Centre, New Delhi 110 025, India /JEOL INDIA PVT. LTD. Hyderabad Office 422, Regus Solitaire Business centre, 1-10-39 to 44, level 4, Gumidelli Towers, Old Airport Road, Begumpet, Hyderabad - 500016, India • **ITALY** /JEOL (ITALIA) S.p.A. Palazzo Pacinotti - Milano 3 City, Via Ludovico il Moro, 6/A 20079 Basiglio(MI) Italy • **KOREA** /JEOL KOREA LTD. Dongwoo Bldg. 7F, 1443, Yangjae Daero, Gangdong-Gu, Seoul, 05355, Korea • **MALAYSIA** /JEOL (MALAYSIA) SDN.BHD. 508, Block A, Level 5, Kelana Business Center, 97, Jalan SS 7/2, Kelana Jaya, 47301 Petaling Jaya, Selangor, Malaysia • **MEXICO** /JEOL DE MEXICO S.A. DE C.V. Arkansas 11 Piso 2 Colonia Napoles Delegacion Benito Juarez, C.P. 03810 Mexico D.F., Mexico • **QATAR** /Mannai Trading Company W.L.L. ALI Emadi Complex, Salwa Road P.O.Box 76, Doha, Qatar • **RUSSIA** /JEOL (RUS) LLC Office 351,,floor 3, 23, Novoslobodskaya St, Moscow 127055, Russia • **SCANDINAVIA** /SWEDEN JEOL (Nordic) AB Hammarbacken 6A, Box 716, 191 27 Sollentuna Sweden • **SINGAPORE** /JEOL ASIA PTE.LTD. 2 Corporation Road #01-12 Corporation Place Singapore 618494 • **TAIWAN** /JIE DONG CO., LTD. 7F, 112, Chung Hsiao East Road, Section 1, Taipei, Taiwan 10023 (R.O.C.) • **THE NETHERLANDS** /JEOL (EUROPE) B.V. Lireweg 4, NL-2153 PH Nieuw-Vennep, The Netherlands • **USA** /JEOL USA, INC. 11 Dearborn Road, Peabody, MA 01960, U.S.A.