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CHARACTERIZATION OF POLYMERS BY MALDI MASS SPECTROMETRY

(March - December 1997)

by

M.H.W. SONNEMANS

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M.H.W. SONNEMANS

Co-worker: R. Fokkens (University of Amsterdam)

Approved by: A.L.C. Smit

Summary

Preliminary results of Matrix-Assisted-Laser-Desorption/Ionization Mass Spectrometry studies on low molecular weight polymers of Carilon, Epoxy Resins and Polystyrenes (500-5000 g/mole) show that this technique appears to be promising in that it combines molecular weight distributions and compositional (end-group) analyses. For high molecular weight polymers, sample preparation is still an issue for further work which should be carried out within a research programme framework.

June, 1998

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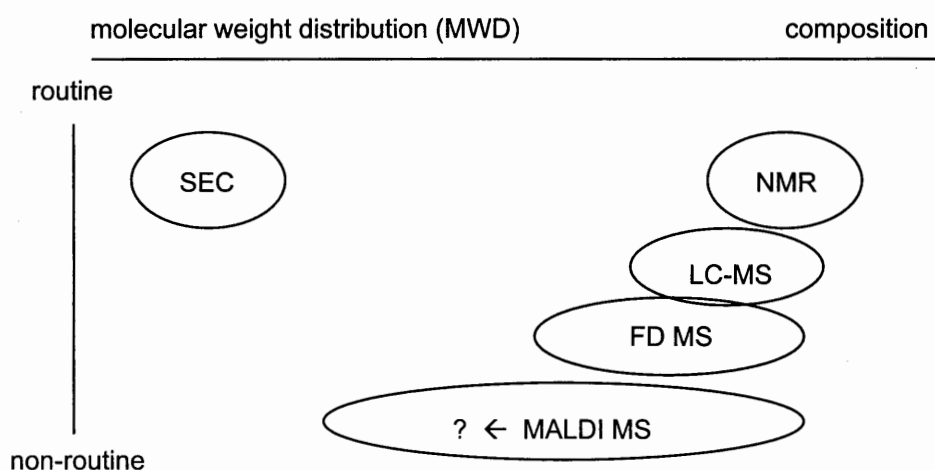
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CHARACTERIZATION OF POLYMERS BY MALDI MASS SPECTROMETRY

1. Introduction

For common in-house applied analyses of polymers several techniques such as Size Exclusion Chromatography (SEC), Infrared Spectroscopy (IR), Nuclear Magnetic Resonance (NMR), Liquid Chromatography (-Mass Spectrometry) and, to a lesser extent, Field Desorption Mass Spectrometry (FD MS) are utilized. Especially SEC and NMR have become routine techniques whereas mass spectrometry is still regarded as a non-routine tool. The advantage and potential of mass spectrometric techniques in polymer analysis is shown below.



Whereas SEC does not give any information on the composition of polymers and NMR does not give any information on the molecular weight distribution (MWD), mass spectrometry has the potential to bridge this gap by its ability to determine end-groups (composition / identification) as a function of polymerization degree. However, the mass range covered so far by LC-MS and FD MS is quite limited, being roughly 200-3000 g/mole, depending on the type of polymer. Furthermore, in-situ reactions of functional groups of the polymers and low sensitivities might hamper the applicability of mass spectrometry over a broader range of molecular weight.

About ten years ago, a new mass spectrometric technique, Matrix-Assisted-Laser-Desorption/Ionization (MALDI), has emerged, proposed for being particularly suitable for bio-organic compounds and bio-polymers¹. As this technique showed superior mass spectrometric performance compared to the conventional mass spectrometric analyses in this area, it became interesting to apply MALDI also to industrial synthetic polymers. Currently, MALDI MS is subject of both academic and industrial interest². The technique has already been firmly established for the analysis of (polar) synthetic polymers such as:

polystyrene (70,000: see text) polyethyleneglycol (30,000) polymethylmethacrylate (30,000) polypropyleneglycol (5,000) polyethyleneterephthalate (5,000) bisphenol-A epoxy resins (5,000) bisphenol-A polycarbonates (5,000)	polyolefin (?) polydiene (?) carilon (?) carilite (?)
--	--

The upper limit of molecular mass for each polymer, in g/mole, established so far is given between brackets. Although polystyrene is actually rather apolar, successful MALDI measurements could have been carried out due to the addition of a small amount of a silver salt (e.g. $\text{Ag}(\text{CF}_3\text{CO}_2)$) to the polystyrene/matrix mixture. In general, the applicability of MALDI MS to the more apolar synthetic polymers such as polyketones, polydienes and polyolefines has not (yet) been investigated.

In attempting to cover information of both the composition and molecular weight distribution by MALDI MS two major obstacles may be encountered in:

1. *Sample preparation.* For MALDI MS a solution of the sample has to be mixed with a suitable matrix (dissolved in the same solvent). After evaporation of the solvent, polymer and matrix molecules are co-precipitated. The function of the matrix is to absorb the laser energy and to transmit energy to the polymer molecules for ionization and desorption from the sample spot (Figure 1). It is essential that the polymer and matrix molecules are in close contact, hence the choice of the matrix is crucial. Commonly applied matrices are organic solid compounds like 1,8,9-anthracenetriol and 2,5-dihydroxybenzoic acid (more matrices are listed in Appendix 1). Since this technique is not (yet) routine, experimental conditions for each series of a particular type of polymer have to be assessed.

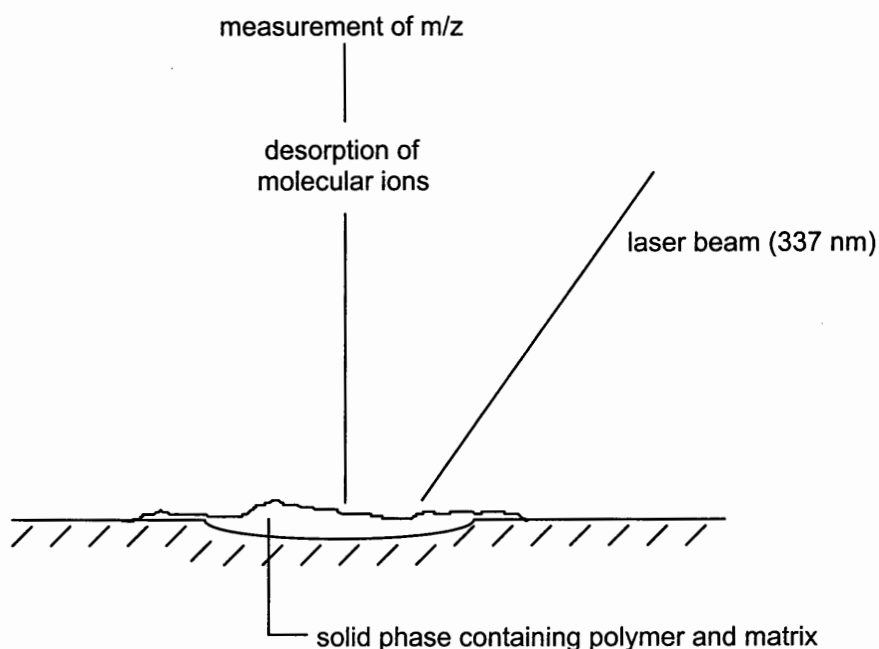


Figure 1: Matrix-Assisted-Laser-Desorption/Ionization (MALDI).

2. *Resolution.* The resolution of a time-of-flight (TOF) mass spectrometer limits the information about the end-groups (hence polymer composition) at higher molecular weights. Depending on the type of monomer and end-groups such information is lost above 5,000 - 10,000 g/mole.

Nevertheless, it is still of interest whether this new technique has potential for analyzing proprietary polymers such as polyketones, epoxy resins, polystyrenes and polystyrene-polybutadiene co-polymers. Since SRTCA has no equipment and only limited experience (EMR-project 1993-1996) with this new technique, collaboration was established with the Institute of Mass Spectrometry at the University of Amsterdam, where some measurements on:

1. low molecular weight Carilon samples,
 2. E1009 epoxy resins and
 3. polystyrene references and polystyrene-polybutadiene di- and triblocks
- have been carried out in 1997. The results of these measurements are discussed in this group report.

2. Experimental

In order to perform MALDI mass spectrometry, a solution of the sample has to be mixed with a suitable matrix (also dissolved). For the polymers reported here, choice of matrix and solvent(s) and their mixing ratios are mentioned in Table 1.

Table 1: Matrices, solvents and mixing ratios used

Polymer / Solvent	Matrix (+ salt) / Solvent	Salt / Solvent	Mixing ratios (v)
LMW Carilon / HF-IPA	Dithranol / HF-IPA (1:1)	Nal / HF-IPA (sat'd sol.)	(1:1:1)
Epoxy Resin / THF (1-10 %w)	Dithranol + Ag(CF ₃ CO ₂) / THF	--	(1:10)
Polystyrene / THF	Dithranol + Ag(CF ₃ CO ₂) / THF	--	(1:3)
Polystyrene-polybutadiene blockpolymers / THF	Dithranol + Ag(CF ₃ CO ₂) / THF	--	(1:3)

LMW = Low Molecular Weight; HF-IPA = HexaFluoro-IsoPropylAlcohol; Dithranol = 1,8,9-anthracenetriol

Two spots of each sample:matrix(:salt) mixture on a gold plate were inserted into the MALDI-TOF equipment (Voyager-DE, PerSeptive Biosystems). Each spot was manually scanned with a pulsed laser beam (N₂-laser: 337 nm, 2 ns pulse width), as shown in Figure 1. Laser intensity was usually set to 60-70% of the maximum power. After each laser pulse the mass range was scanned several times (TOF linear and reflectron modes and using delayed extraction). All mass spectra were accumulated to enhance signal-to-noise ratio. Good mass spectra were obtained when the laser beam hit a local high concentration of the polymer:matrix:cation which had to be found by trial and error. Especially the use of apolar solvents such as HF-IPA made this more labour intensive since the spots had been spread out extensively. Unfortunately, the software does not provide a mass - intensity table which precludes an accurate calculation of M_n and M_w sofar.

3. Results

3.1 Low Molecular Weight Carilon

Figure 2a shows a MALDI mass spectrum of a low molecular weight Carilon polymer sample (SP19A). The distance between two peaks is 56 ($\text{CH}_2\text{CH}_2\text{CO}$ monomer m) and it appears that the molecular weight envelope consists of actually three MWD's, roughly ranging from (i) 300-600, (ii) 600-1600 and (iii) 1600-2400. Especially in the first region more species are present as can be seen from interfering peaks. The global MWD as obtained by MALDI MS agrees fairly well with the MWD as determined by SEC. Looking into more detail (Figures 2b-2d) more molecular information can be obtained. First, each peak in Figure 2a consists of actually three peaks (disregarding the ^{13}C isotopic peaks) which reflect the following three end-group combinations of a Carilon polymer:

keto-keto	$\text{C}_2\text{H}_5\text{CO}-(m)_n-\text{C}_2\text{H}_5$	mass = $(86+23) + 56n$
keto-ester	$\text{C}_2\text{H}_5\text{CO}-(m)_n-\text{OCH}_3$	mass = $(88+23) + 56n$
ester-ester	$\text{CH}_3\text{OCO}-(m)_n-\text{OCH}_3$	mass = $(90+23) + 56n$

Since the Carilon molecular ions are formed by cationization (Na^+ complexes), the mass of the end-group is increased by 23 (Na^+). Assuming that there is no discrimination in response the relative abundance of each species reflects their actual concentration as a function of polymerization degree! In fact, the ester/keto ratio increases with increasing monomer number (n), as has also been concluded from earlier NMR and FD MS work³. Compared to FD MS, the MALDI MS results appear to be more accurate and reliable since no thermally induced formation of furan groups occurs. Moreover, the mass range covered by MALDI, 300 - 3000, is larger than that of FD, 600 - 1500. Based on the mass spectrometric resolution achieved so far, it is estimated that no qualitative and quantitative information on the various end-group combinations can be obtained beyond 3000 g/mole. Some of the interfering peaks in the 300 - 700 mass region have been assigned to the catalytic bis-(diphenylphosphine)-Pd complex, $[(\text{C}_6\text{H}_5)_2\text{P}-(\text{CH}_2)_3-\text{P}(\text{C}_6\text{H}_5)_2]\text{Pd}^+$; mass = 518.9 (Figure 2e), and its $\text{Na}_x\text{I}_{1+x}$ complexes, produced during the MALDI process. The nature of the catalytic complex left behind in the polymer sample can thus simultaneously be determined.

Figures 3a-e show similar MALDI mass spectra of another low molecular weight Carilon (SP23A). Assignment of the masses is equal to the previous sample. However, a direct comparison of these spectra with those of the previous, reveals that this sample (i) consists of only one MWD, (ii) is more skewed to the lower end and (iii) contains more keto-ester and less ester-ester end-groups. Furthermore, the catalytic bis-(di(*ortho*-methoxyphenyl)-phosphine)-Pd complex, $[(\text{C}_6\text{H}_4\text{OCH}_3)_2\text{P}-(\text{CH}_2)_3-\text{P}(\text{C}_6\text{H}_4\text{OCH}_3)_2]\text{Pd}^+$; mass = 639.0 (Figure 3e), could unequivocally be identified.

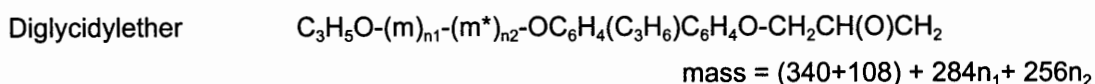
3.2 Epoxy Resins

A method on performing MALDI MS on epoxy resins has already been reported in the literature⁴. MALDI mass spectra of an epoxy resin (E1009 LLE) show molecular masses up to 6000, corresponding roughly to $n = 20$ (Figure 4a). The distance between two peaks is 284 which is equal to the mass of the diphenylolpropane-isopropanol monomer m ($\text{OC}_6\text{H}_4(\text{C}_3\text{H}_6)\text{C}_6\text{H}_4\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2$). However, compared to LC-data it has to be concluded that also with MALDI MS the lower end of the resin ($1 < n < 20$) is covered, hence, representing only a fraction of the total sample. Diglycidylethers and their mono- α -glycols are dominantly present; the phenol-glycidylethers to a less extent (Figure 4b).

Diglycidylether	$\text{C}_3\text{H}_5\text{O}-(m)_n-\text{OC}_6\text{H}_4(\text{C}_3\text{H}_6)\text{C}_6\text{H}_4\text{O}-\text{CH}_2\text{CH}(\text{O})\text{CH}_2$	mass = $(340+108) + 284n$
mono- α -glycol	$\text{C}_3\text{H}_5\text{O}-(m)_n-\text{OC}_6\text{H}_4(\text{C}_3\text{H}_6)\text{C}_6\text{H}_4\text{O}-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$	mass = $(358+108) + 284n$
phenol-glycidylether	$\text{H}-(m)_n-\text{OC}_6\text{H}_4(\text{C}_3\text{H}_6)\text{C}_6\text{H}_4\text{O}-\text{CH}_2\text{CH}(\text{O})\text{CH}_2$	mass = $(284+108) + 284n$

The molecular ions are formed by cationization (Ag^+ complexes), hence, the mass of the end-group is increased by 108 (Ag^+). Assuming that there is no discrimination in response the relative abundance of each species reflects their actual concentration. This may facilitate current assignments of LC-peaks to specific resin compounds.

Similar MALDI mass spectra (Figure 5a and 5b) of low molecular weight compounds have been obtained for another epoxy resin (E1009 L). Assignment of the masses is equal to the previous resin. In this sample, the diglycidylethers with even monomer number (n) are dominantly present. Furthermore, diglycidylethers with odd n , phenol-glycidylethers and nonylphenol-glycidylethers were detected. Moreover, due to the fact that the resins could be measured up to a mass of 5,000 g/mole, one was able to determine that the concentration of the diglycidylethers of this resin decreases at the expense of a new resin type, consisting of a mixture of two monomers having masses 284 (m) and 256 (m^*) (Figure 5c).



Based on this it was tentatively concluded that also a slight amount of diphenylolmethane (diphenylolmethane-isopropanol monomer m^* : $\text{OC}_6\text{H}_4(\text{CH}_2)\text{C}_6\text{H}_4\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2$) was included.

3.3 Polystyrenes and Polystyrene-Polybutadiene di- and triblocks

Attempts to measure polystyrene-(*hydrogenated*)polybutadiene di- and triblocks (25,000-50,000 g/mole total molecular weight) using MALDI MS, failed so far. Experimental MALDI conditions were established on polystyrene standards, which in contrast were quite easy to measure even up to molecular weights of 70,000 g/mole (Figure 6a-c). The distance between two peaks is 104 ($\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$ monomer m) and the masses shown in these figures are assigned following:



The molecular ions are formed by cationization (Ag^+ complexes), hence, the mass of the end-group is increased by 108 (Ag^+). The estimated number average molecular weights were in good agreement with the reported ones up to 20 kg/mole (Figure 7). At higher molecular weights the MALDI MS yields somewhat higher number average molecular weights (+15 to +20 %). At such high molecular weights no information on end-groups can be obtained.

Since under the same conditions no signals of polystyrene-(*hydrogenated*)polybutadiene di- and triblocks (containing 17 to 20 %mole styrene) have been found, it is thought that during sample preparation the blockpolymer chains remain entangled whereas at similar concentrations polystyrene chains are virtually disentangled.

4. Discussion

The preliminary MALDI MS results are encouraging by showing that up to molecular weights of 4,000 g/mole (Carilon, epoxy resins) or to 10,000 g/mole (polystyrenes), molecular weight distributions as well as chemical/molecular information can be obtained. This is clearly an improvement compared to current in-house mass spectrometric techniques. However, attempts to obtain molecular information beyond 10,000 g/mole have not been successful which is most likely due to sample preparation. The necessity to have polymer molecules well-dissolved in both the solvent and homogeneously distributed in the solid matrix, limits till now the proper analysis of high molecular weights polymers.

Looking more into detail it is suggested that in order to obtain polymer and matrix molecules in close proximity

1. polymers have to be entirely dissolved before their solution is mixed with the matrix solution
2. during evaporation of the solvent of the mixture, polymer and matrix molecules must not segregate (homogeneous distribution of polymers throughout the solid matrix)

Ad 1. One explanation for the absence of high molecular weight compounds in the MALDI mass spectrum might be that the desorption of these compounds from the matrix is hampered by entanglement of the polymer chains. Compared to the rather packed conformation of a bio-organic peptide chain in e.g. water (coiled helices), the conformation of synthetic apolar polymer chains in an organic solvent is more or less of a clew type, entangled with each other. Remedies to obtain individual disentangled polymer chains include the use of better solvents and diluted solutions. In Table 2 some other matrices, solvents and mixing ratios are proposed, these being based on discussions and literature.

In case of the hydrogenated polydienes it is suggested to look at the unsaturated precursors for molecular weight distribution assuming that this distribution would not have been changed during hydrogenation. Recent studies reported the determination of polybutadienes and polyisoprenes up to 25,000 g/mole using other matrices and cations^{5,6}.

Table 2: Matrices, solvents and mixing ratios proposed

Polymer / Solvent	Matrix (+ salt) / Solvent	Salt / Solvent	Mixing ratios (v)
Resins / THF:water (1-5%w)	Dithranol / THF (10 %w)	Ag(CF ₃ CO ₂) / THF (sat'd sol.)	(1:10-100:1)
Resins / THF:glycol (1 %w)	Dithranol / THF (10 %w)	Ag(CF ₃ CO ₂) / THF (sat'd sol.)	(1:10-100:1)
Polydienes / THF (0.5 %w)	<i>all-trans-retinoic acid</i> / THF (0.15 M)	Cu(NO ₃) ₂ / water (0.1 M)	(1:100:1)
Polydienes / THF (10 ⁻⁴ M)	POPOP / THF (sat'd sol.)	Ag(acac) / THF (sat'd sol.)	(1:10:1)

⁶POPOP: 1,4-di-(2-(5-phenyloxazolyl))benzene

Ad 2. Even though one would have been able to dissolve each polymer chain without any entanglement, it is of importance that the chains are then well mixed with the matrix molecules and remain well mixed during solvent evaporation. Otherwise this will lead to poor spot-to-spot signal repeatability and poor sample-to-sample reproducibility, frequently encountered. Co-precipitation can be achieved, not only by a proper choice of the matrix, but also by adding surfactants⁷ or using spray deposition⁸. An alternative would be use of high viscosity liquid matrices⁹. Evidently, for each polymer type a tailored method is required.

The opportunity to measure molecular weights directly by MALDI MS is promising. However, especially for polydisperse polymers the molecular weight distribution obtained by MALDI MS often deviates from the distribution obtained by e.g. SEC. It is thought that during MALDI MS the larger polymers within a broad range of molecular weights are somewhat more hampered in desorption and ionization compared to the smaller ones. By taking monodisperse fractions from SEC a more accurate estimate of the molecular weight of each fraction can be established by MALDI MS¹⁰.

The costs of a MALDI MS measurement strongly depends on whether a valid method is available or not. For polystyrenes and polyethyleneglycols, as published often in the literature, and low molecular weight polyketones and resins, a simple measurement can be run quickly. For other polymers for which methods have to be developed (sample preparation, choice of matrix etc.), costs will be higher. Especially for optimising sample preparation every suggestion addressing the issues as discussed may be of help in achieving reliable and accurate information on a shorter term.

5. Conclusions

Results of MALDI MS studies on low molecular weight Carilon and resins as well as on polystyrenes show that this technique appears to be promising. It has been demonstrated that certainly for low molecular weight polymers the data obtained combine molecular weight distributions with end-group analyses (composition) provided a method of sample preparation is known and/or validated. For high molecular weight polymers, sample preparation is still an issue for further work which should be carried out in a customer-oriented research programme.

Amsterdam, June 1998

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Appendix 1**Common Matrices in MALDI MS**

DHB	2,5-DiHydroxyBenzoic acid
Dithranol	1,8,9-anthracenetriol <i>all-trans</i> -retinoic acid sinapinic acid
α -CCA	α -Cyano-4-hydroxyCinnamic Acid
IAA	<i>trans</i> -3-IndoleAcrylic Acid
POPOP	1,4-di-(2-(5-phenyloxazolyl))benzene



MALDI-TOF

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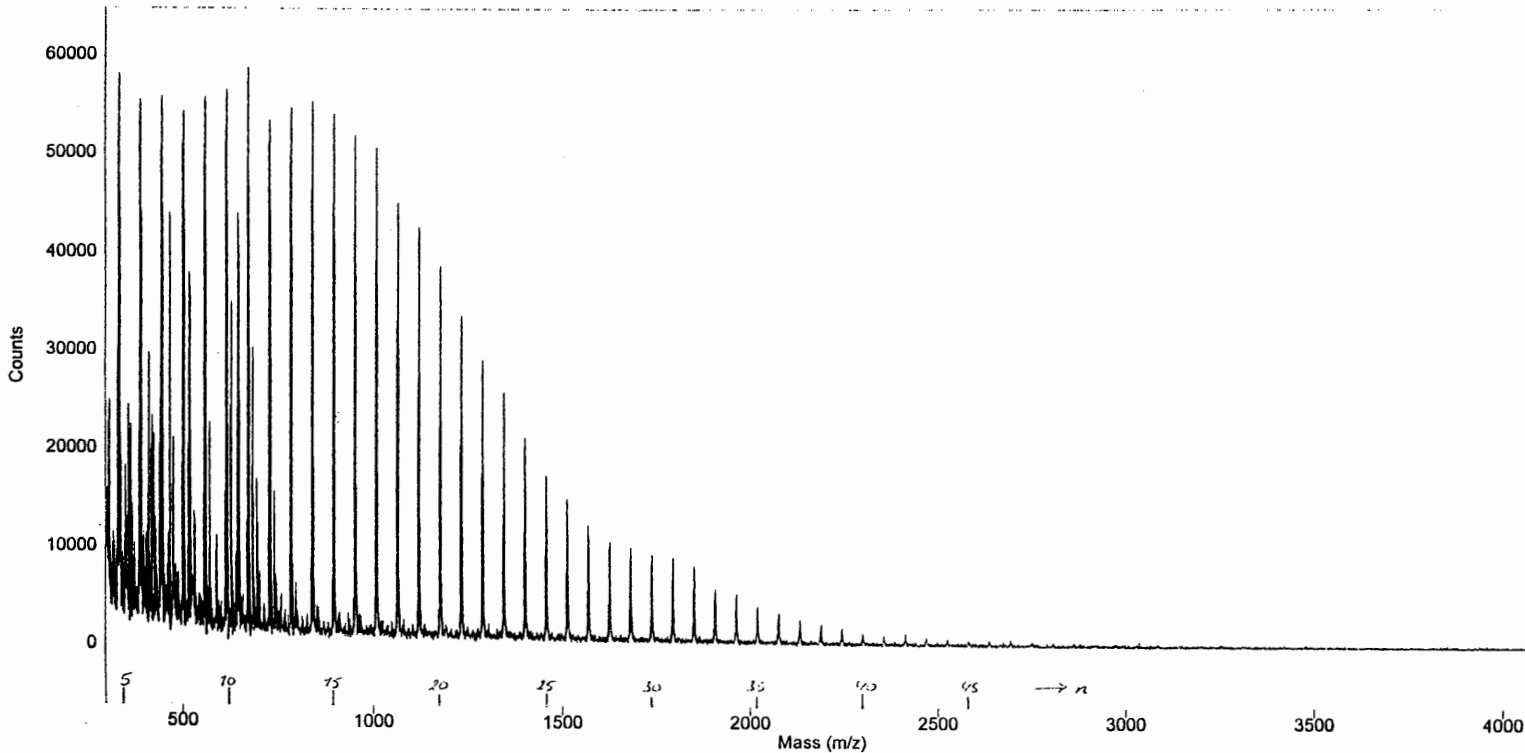


Figure 2a

MALDI mass spectrum of a low molecular weight Carilon sample (SP19A):
(a) total mass spectrum: $5 < n < 45$.

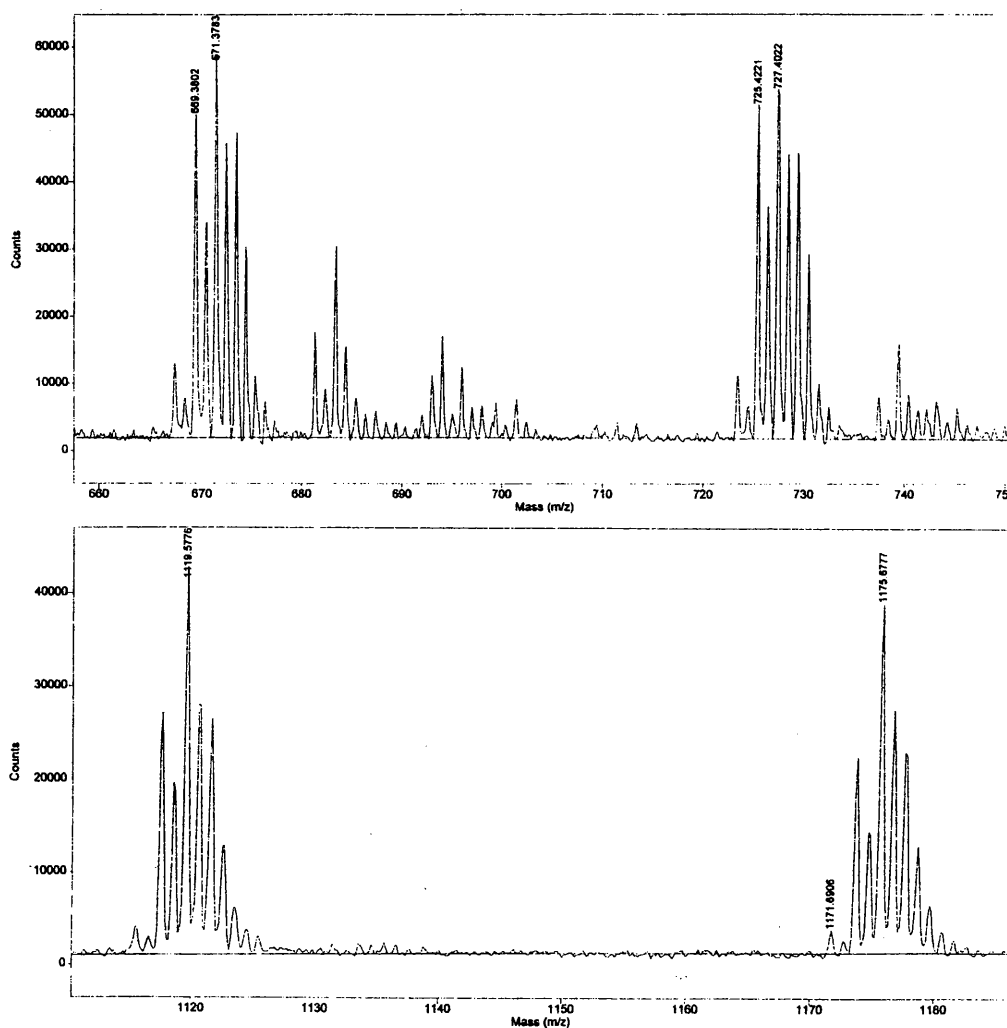
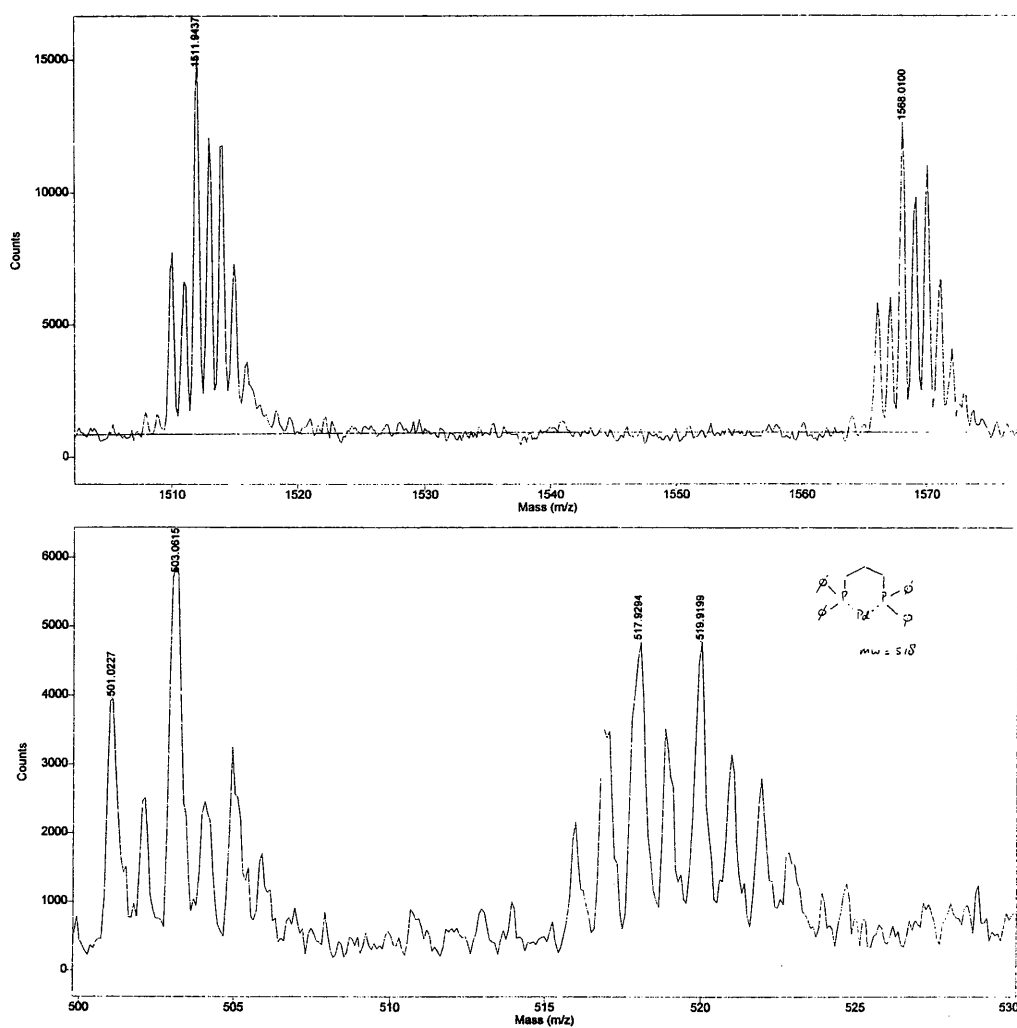


Figure 2b-c

MALDI mass spectrum of a low molecular weight Carilon sample (SP19A):

(b) detail for $n = 11 - 12$,

(c) detail for $n = 19 - 20$.

**Figure 2d-e**

MALDI mass spectrum of a low molecular weight Carilon sample (SP19A):
(d) detail for $n = 26 - 27$,
(e) detail on the catalytic bis-(diphenylphosphine)-Pd complex.



MALDI-TOF

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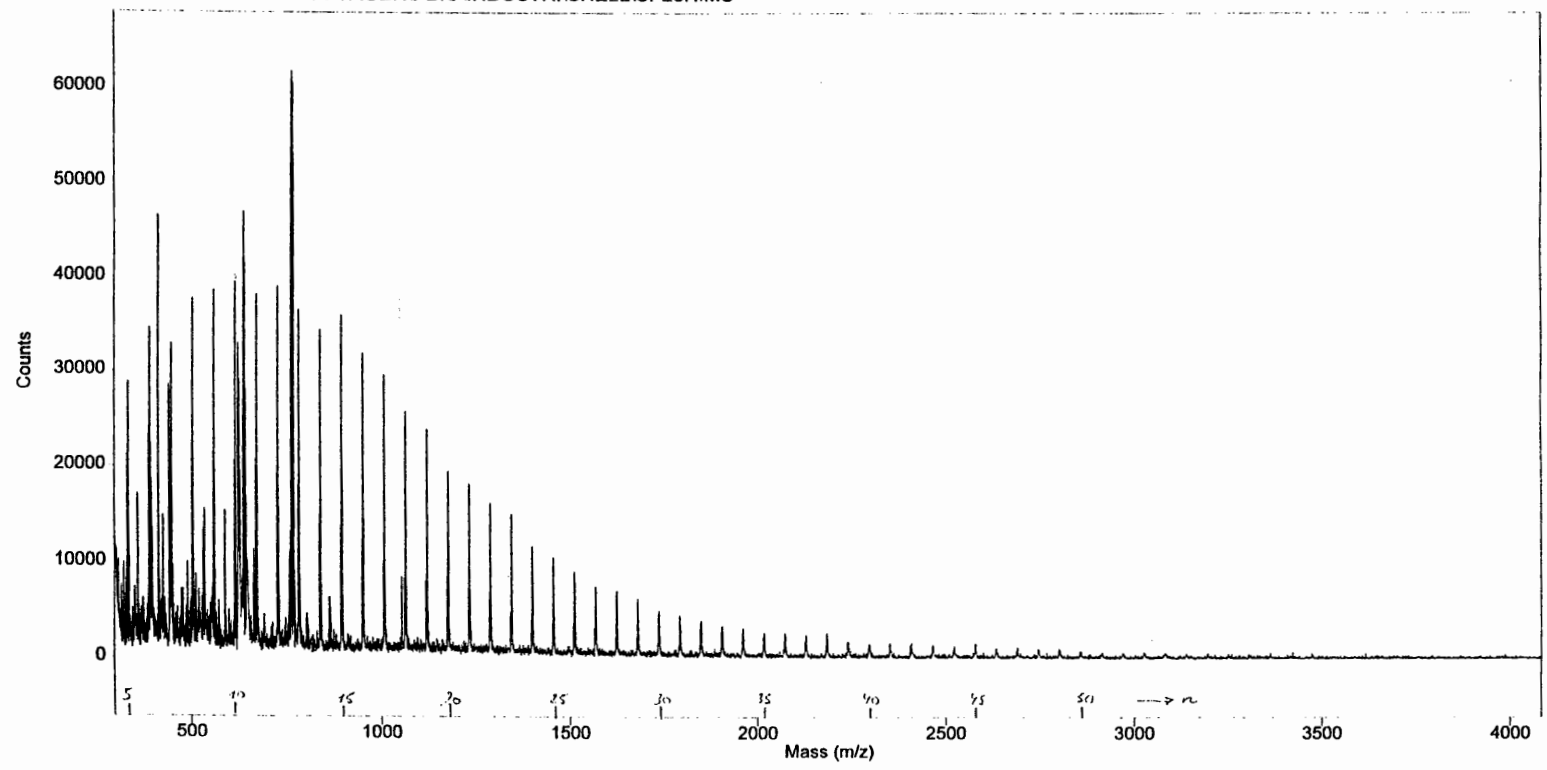


Figure 3a

MALDI mass spectrum of a low molecular weight Carilon sample (SP23A):
(a) total mass spectrum: $5 < n < 50$.

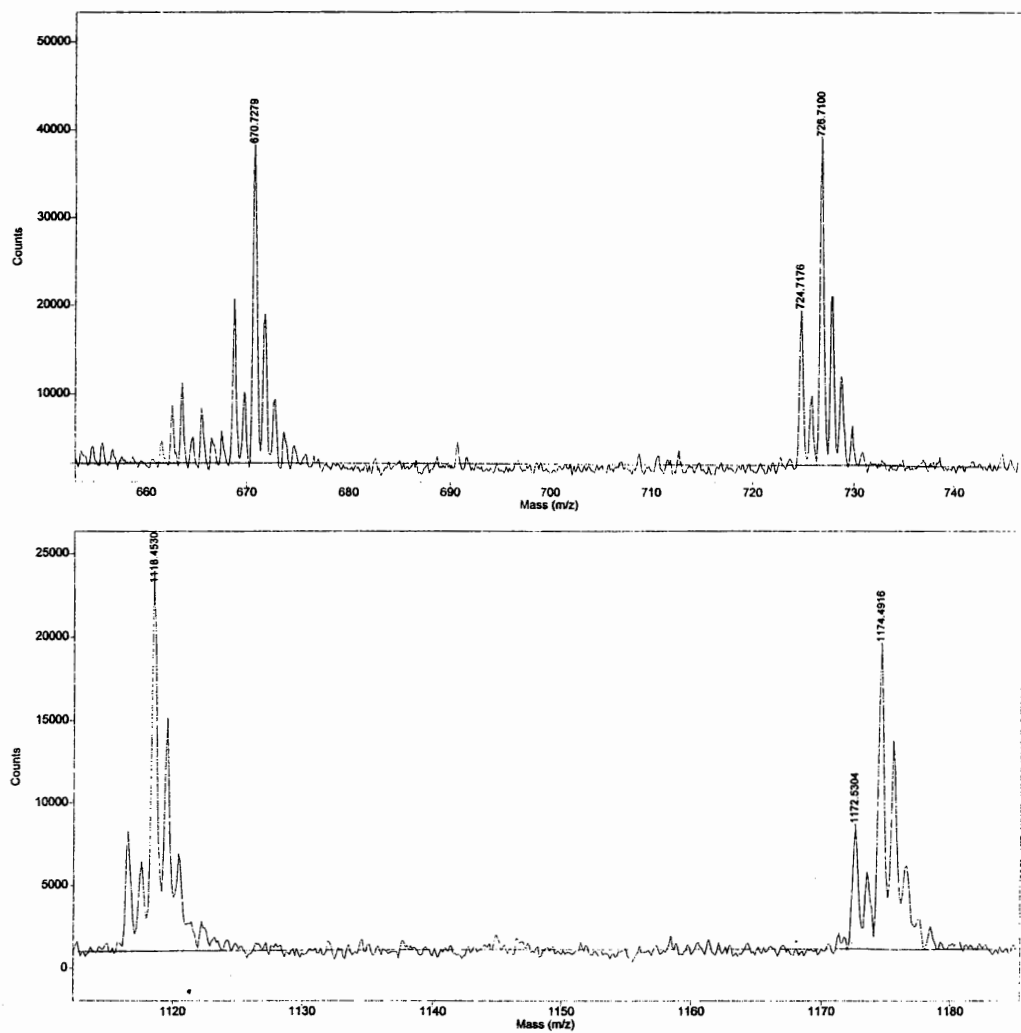
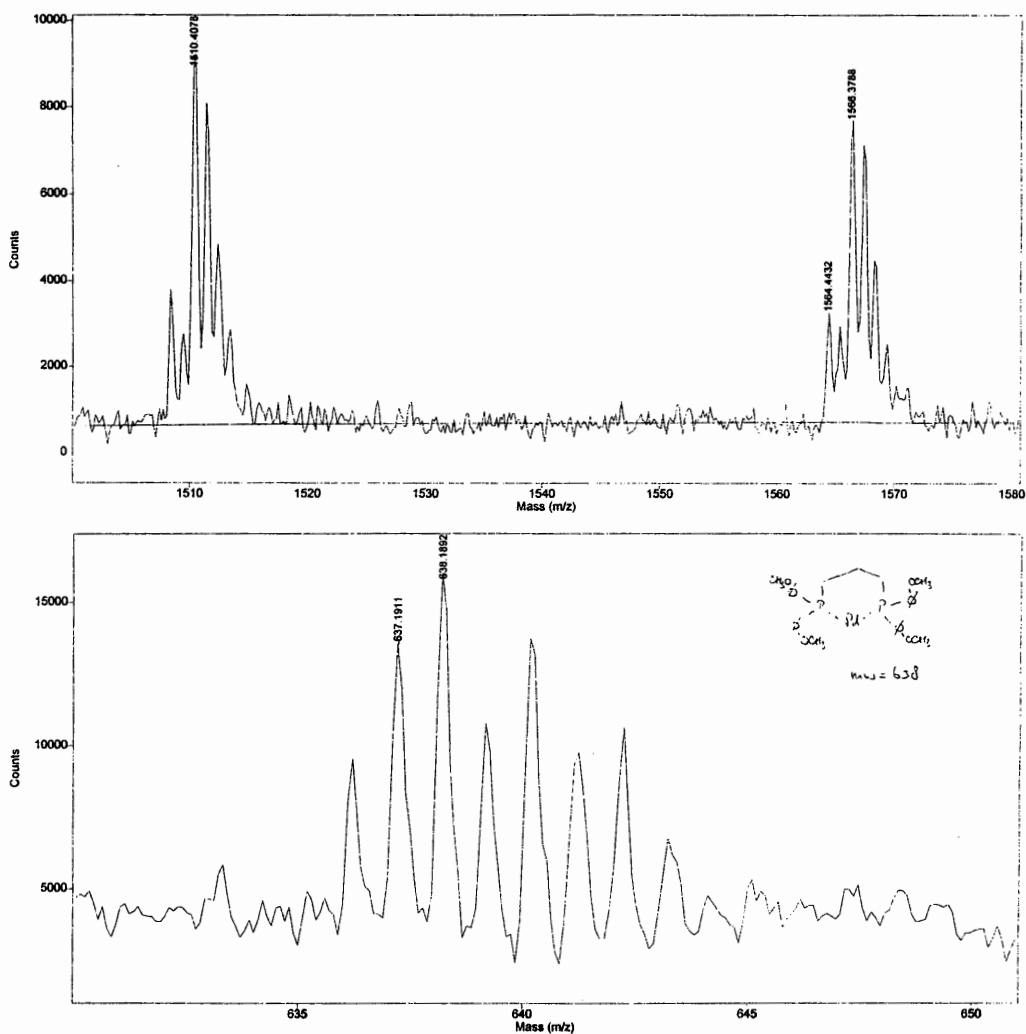


Figure 3b-c

MALDI mass spectrum of a low molecular weight Carilon sample (SP23A):

(b) detail for $n = 11 - 12$,

(c) detail for $n = 19 - 20$.

**Figure 3d-e**

MALDI mass spectrum of a low molecular weight Carilon sample (SP23A):

(d) detail for $n = 26 - 27$,

(e) detail on the catalytic bis-(di(*ortho*-methoxyphenyl)phosphine)-Pd complex.



MALDI-TOF

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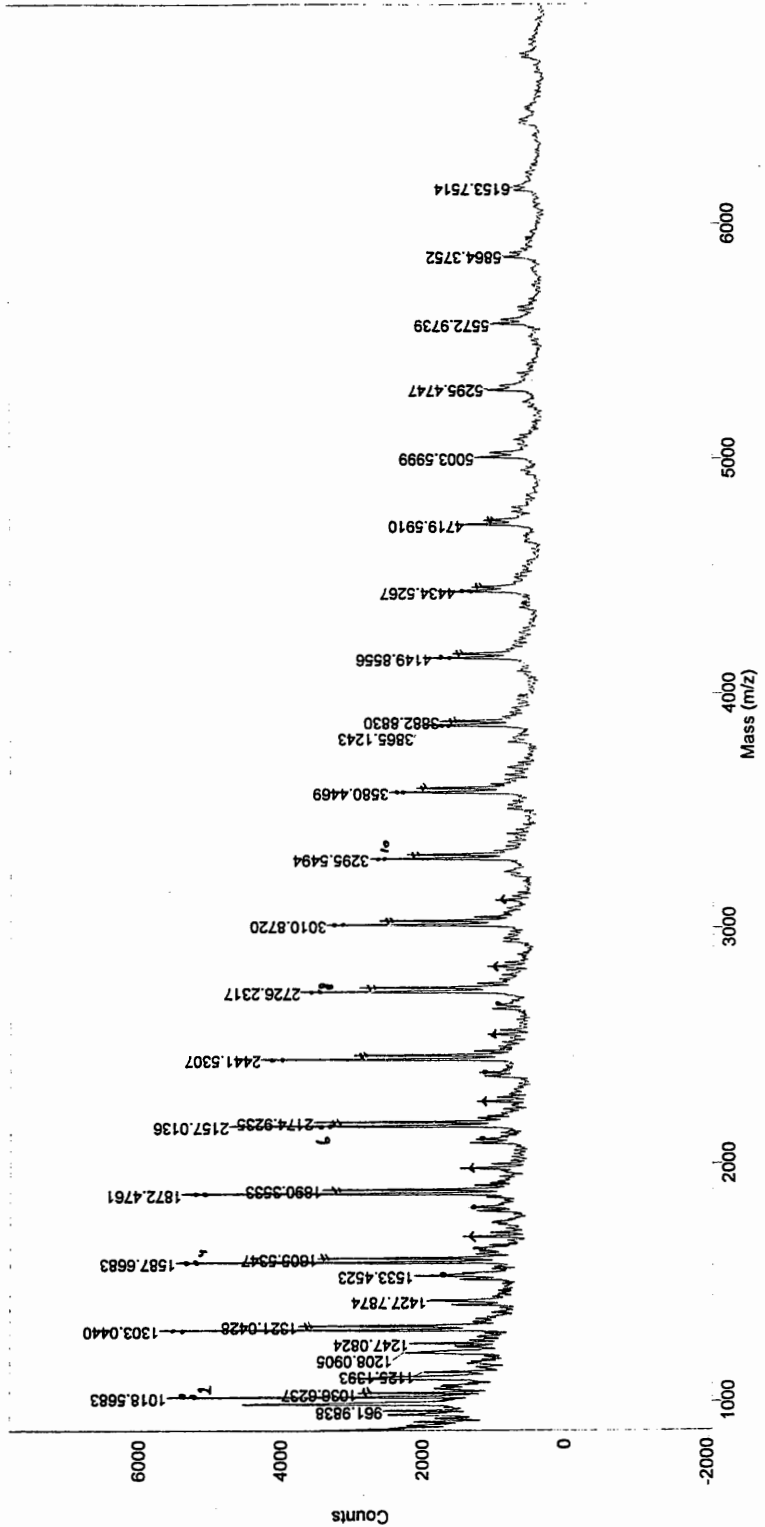


Figure 4a
MALDI mass spectrum of resin E1009 LLE: (a) total mass spectrum: 2 < n < 20.



MALDI-TOF

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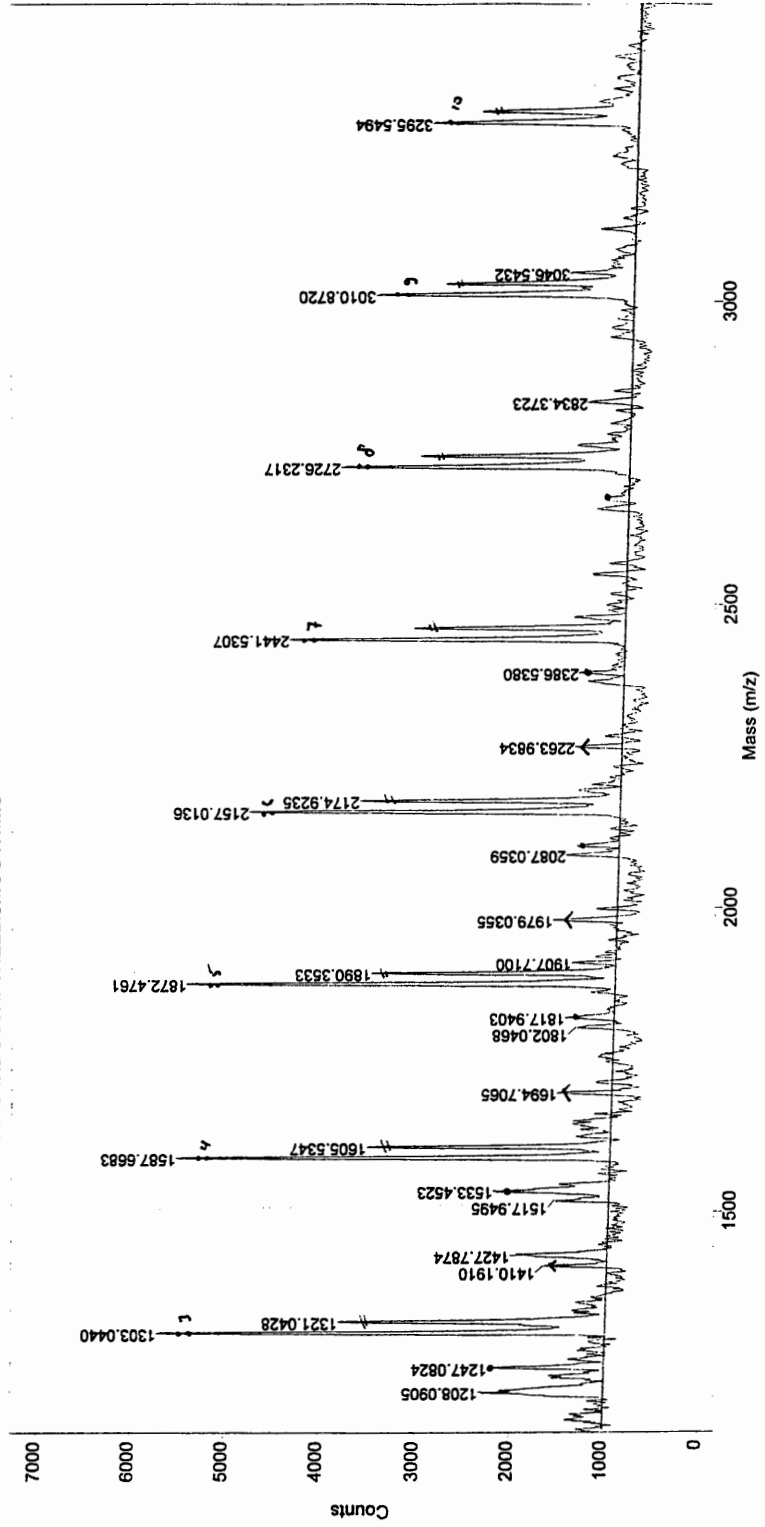


Figure 4b

MALDI mass spectrum of resin E1009 LLE: (b) detail for n = 3 - 10.



MALDI-TOF

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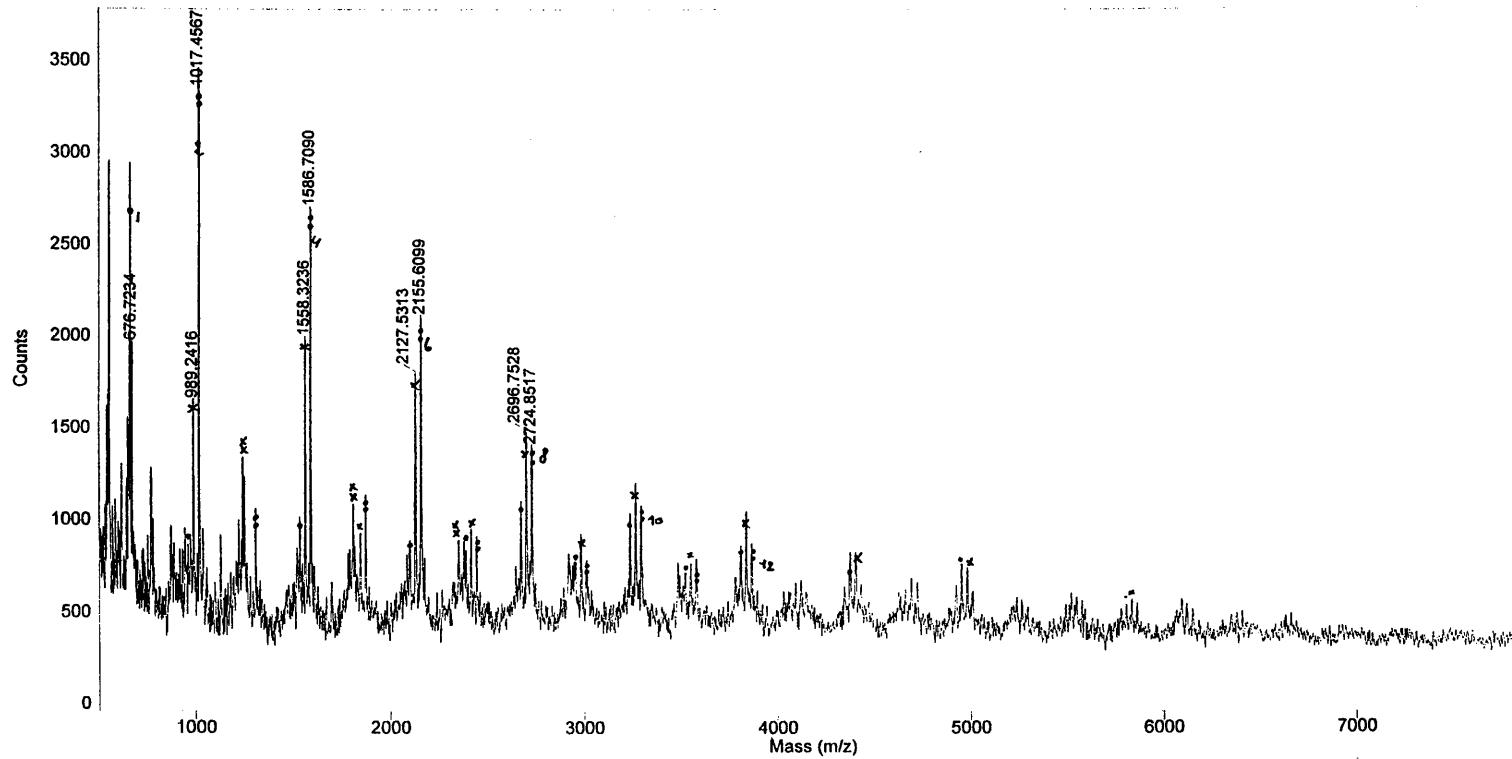


Figure 5a

MALDI mass spectrum of resin E1009 L: (a) total mass spectrum: $5 < n < 20$.



MALDI-TOF

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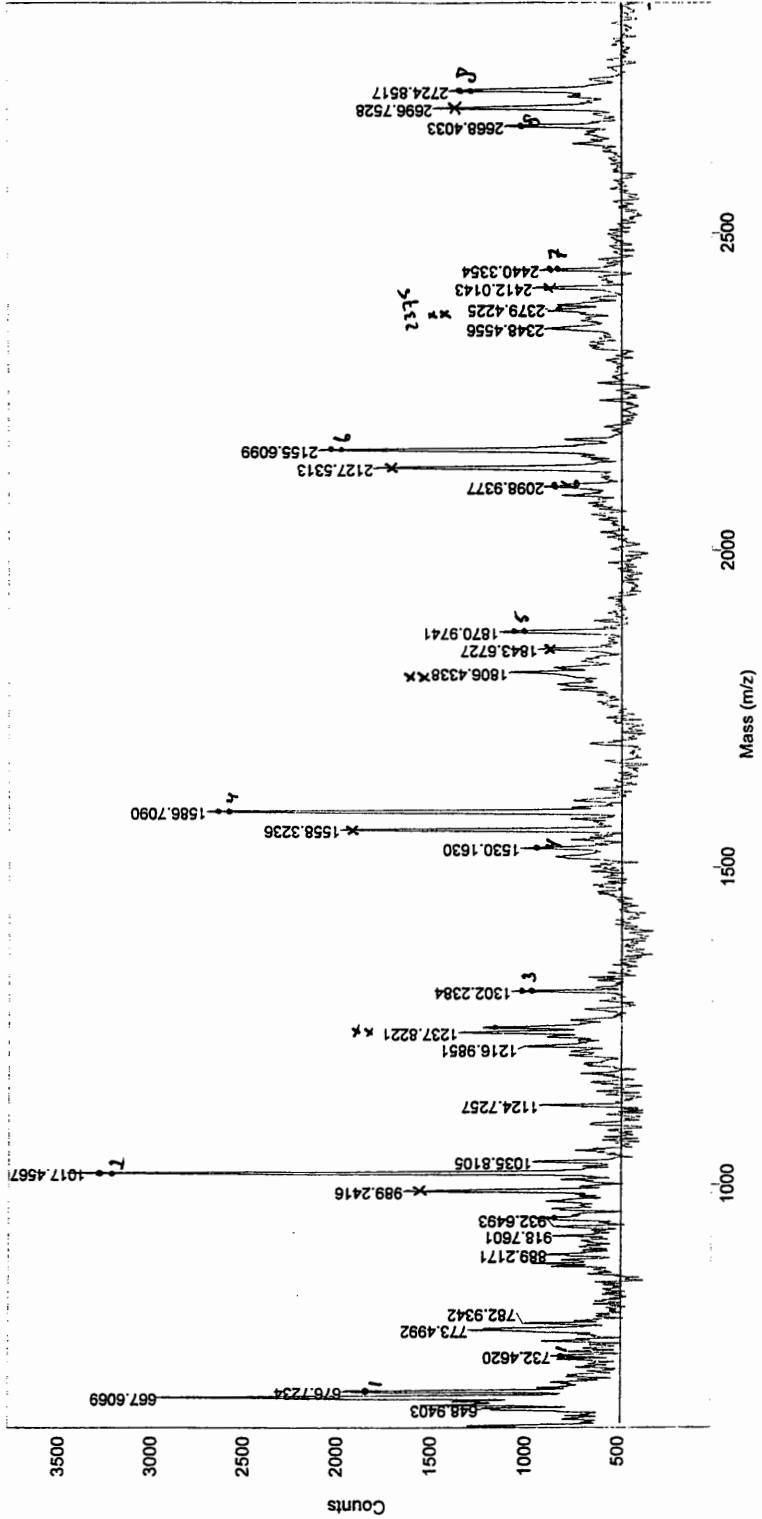


Figure 5b

MALDI mass spectrum of resin E1009 L: (b) detail for n = 2 - 8.



MALDI-TOF

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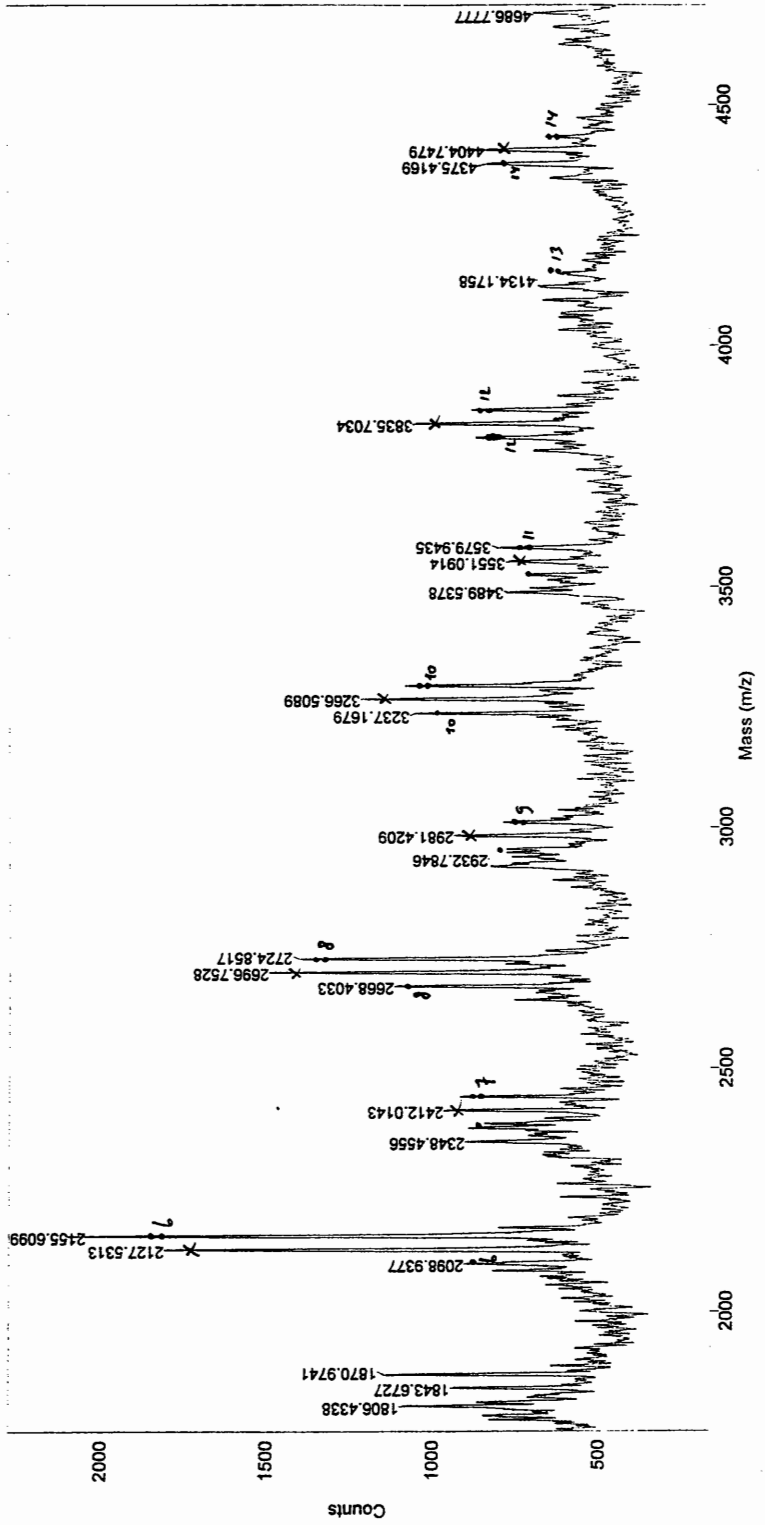


Figure 5c

MALDI mass spectrum of resin E1009 L: (c) detail for n = 6 - 14.



MALDI-TOF

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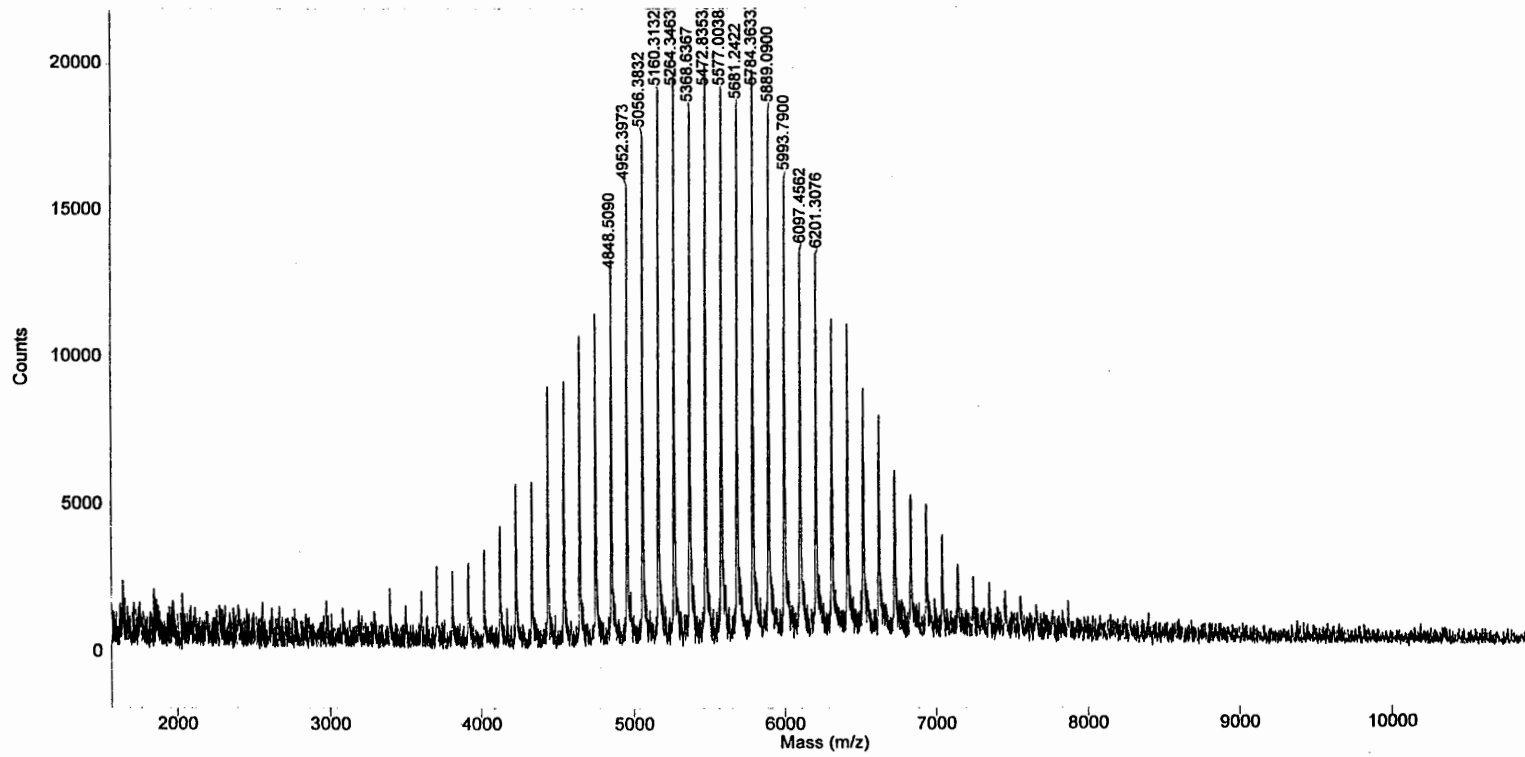


Figure 6a

MALDI mass spectrum of polystyrenes: (a) $\langle M_n \rangle = 5250$.



MALDI-TOF

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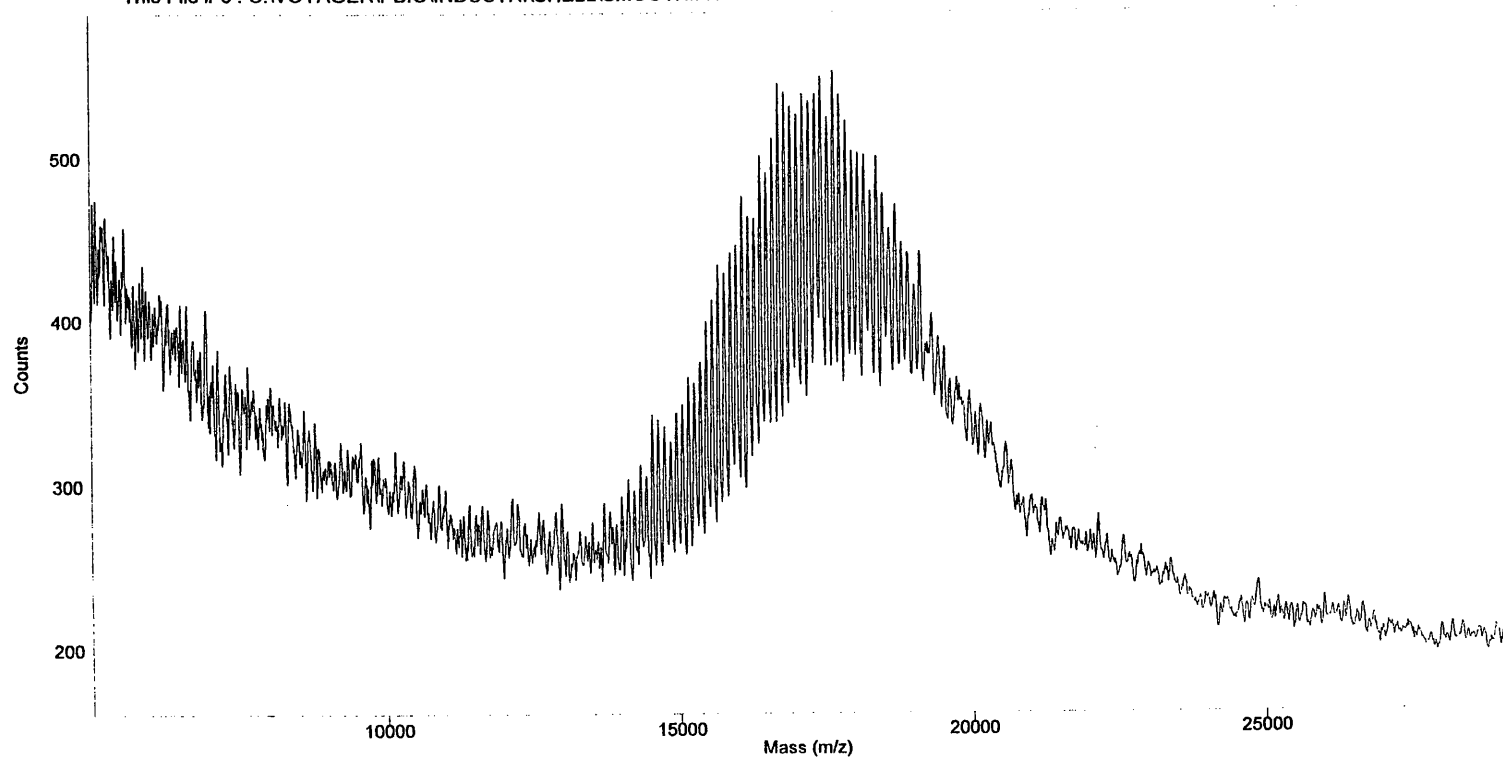


Figure 6b

MALDI mass spectrum of polystyrenes: (b) $\langle M_n \rangle = 18400$.

List of Symbols

$\langle M_n \rangle$ number average Molecular weight

List of Abbreviations

FD MS	Field Desorption Mass Spectrometry
IR	InfraRed spectroscopy
LC-MS	Liquid Chromatography - Mass Spectrometry
LMW	Low Molecular Weight
MALDI	Matrix Assisted Laser Desorption Ionization
MS	Mass Spectrometry
MWD	Molecular Weight Distribution
NMR	Nuclear Magnetic Resonance
SEC	Size Exclusion Chromatography

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