Analysis of Polymer Additives by Matrix-Assisted Laser Desorption Ionization/Time of Flight Mass Spectrometer Using Delayed Extraction and Collision Induced Dissociation

Shih Tsung Hsiao (蕭世宗), Mei Chun Tseng (曾美郡),
Yet Ran Chen (陳逸然) and Guor Rong Her* (何國榮)
Department of Chemistry, National Taiwan University, Taipei, Taiwan, R.O.C.

Matrix-assisted laser desorption/ionization (MALDI) in combination with mass spectrometry proved to be a viable method for identifying additives in polyethylene extracts. The MALDI mass spectra of additives standards were found to be very simple consisting of $[M+H]^+$ and/or $[M+Na]^+$ pseudo molecular ions with little fragment ions. For real samples, which often contain more than one additive, the production of only one or two ions for each additive makes the tentative assignment much easier. Collision induced dissociation (CID) of the pseudomolecular ion is used to confirm the tentative assignment. The analysis of high molecular weight additives, such as Chimassorb 944 and Tinuvin 622 indicated that MALDI was superior to other ionization techniques such as electrospray ionization (ESI), desorption chemical ionization (DCI) and fast atom bombardment (FAB) in the analysis of high molecular weight polymer additives. Sample preparation was found to be more critical than DCI in the analysis of real sample. The signals were interfered by the low molecule weight polyethylene molecules, which were co-extracted with the additives. This problem was partially overcome by using acetone instead of methanol to precipitate the low molecular weight polyethylene molecules.

INTRODUCTION

The range of applications of polymeric materials is extending at an amazing rate and the number of additives available to modify polymer properties is increasing proportionately. These additives include antioxidants, UV stabilizers, Lubricants etc. The failures of products can often be attributed to the leaching of additives from polymer, the chemical transformation of certain additives and the omission of essential additives during the manufacturing processing. Moreover, some additives are known as potential health hazards.[1] Therefore, reliable and rapid analytical methods are often needed for the identification of unknown additives in polymers and/or monitoring the stability of additives during processing or services.

Direct spectroscopic methods such as ultraviolet absorption, infrared, fluorescence, and X-ray fluorescence have been reported.[2-5] The main disadvantage of the spectroscopic techniques is a lack of specificity. A more desirable approach requires extraction of the additives following by off- or on-line chromatographic separation and spectroscopic identification.[6-10] These methods are generally time consuming.

Analysis of polymer additives by mass spectrometry and its related techniques enhanced the capability of compound identification. Moving toward higher molecular weight additives with less volatility, conventional MS techniques such as electron ionization (EI), chemical ionization (CI) and GC-MS are generally not suitable for their analysis. Thus, soft ionization techniques such as field desorption, fast atom bombardment (FAB),[11,12] desorption chemical ionization (DCI),[13,14] laser desorption,[15-20] electrospray ionization (ESI)[21] and atmospheric pressure chemical ionization (APCI)[22,23] all have been investigated for their utility in the analysis of polymer additives either in polymer extracts or directly from polymer matrices.

Earlier studies from our laboratory suggested that DCI in combination with low and high energy CID was capable of detection polymer additives in polyethylene without prior chromatographic separation.[13,14] While DCI is quite useful to the analysis of a variety of additives, it does have limited capability in the analysis of high molecular weight additives.[13,14] Since its development, matrix-assisted laser desorption/ionization (MALDI) has been widely used as a soft ionization technique for very large molecules. Furthermore, MALDI is known to have less matrix effect in comparison with FAB or ESI. However, despite its capability in the analysis of high

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* Corresponding author. Tel: +886-2-23690152 ext. 109; Fax: +886-2-23638058

mo lec u lar weight com pounds, there have been very few reports on the anal y sis of poly mer ad di tives by MALDI.[24,25] In ad di tion, these re ports were also lim ited to a few ad di tives. Scrivens et al. re ported the anal y sis of poly mer ad di tives using dithranol as ma trix and add ing siliver trifluoroactate to form siliver ad ducts.[24] The sig nals were re ported to be not very re pro duc ible. The siliver adduct ap proach has also been used by Kornfeld et al. in a poster pre sented at 1997ASMS conference.[25] A more ex ten sive study in clud ing the use of delayed ex trac tion, post source de cay (PSD) and CID in the anal y sis of poly mer ad di tives by MALDI was per formed in this lab o ra tory. The mer its and lim i ta tions of the ap proach are re ported.

EXPERIMENTAL

Chemicals

Ad di tives stan dards were kindly pro vided by Ciba-Geigy (Tai wan). Ox i dized Naugard 524 was pre pared by ox i-da tion of Naugard 524 with hy dro gen per ox ide. The structures and triv ial names of the ad di tives pre sented in this work are shown in Ta ble 1. The poly eth yl ene sam ples were obtained from lo cal sup pli ers. 1,8-Dihydroxy-9-anthracenone (Dithranol) and 4-Hydroxy-3-methoxycinnamic acid (Ferulic acid) were purchased from Sigma (St. Louis, MO). 2,5-dihydroxybenzoic acid (2,5-DHB) was from Aldrich (St. Louis, MO). Tetrahydrofuran (THF) was from Riedel-de Haen (Ger many). An a lyt i cal grade ac e tone, meth a nol and to-lu ene were sup plied by Lab-scan (Dub lin, Ire land).

Sample Preparation

Ad di tives and ma trix were dis solved in tetrahydrofuran (THF) to make *ca*. 10 mg/mL so lu tions. The sam ple so lu tion and the ma trix so lu tion were mixed 1:10 (v/v), and 1 μL of the mix ing so lu tion was spot ted on the sam ple plate and dried in the air.

Polymer Extract

A weighted Poly eth yl ene sam ple (ca.1 g) was refluxed with 100 mL of to lu ene in a 250-mL round-bottomed flask for 3 h. Af ter cool ing, 20 mL of ac e tone was added to pre cip i-tate low mo lec u lar weight poly mer. The ex tract so lu tions were fil tered and dried by purg ing with ni tro gen gas.

Mass Spectrometry

MALDI was per formed on a PerSeptive Voy ager DE-RP time of flight (TOF) mass spec trom e ter (Framingham, MA, USA). This sys tem is equipped with a N_2 la ser (337 nm). For CID and PSD anal y sis, the pre cur sor ions were se lected us ing the timed ion se lec tor at a res o lu tion of about 50. For CID ex per i ments, the col li sion cell was filled with air un til the pres sure in the source cham ber reached ap prox i mately $3.5\times10^{-6} \sim 5\times10^{-6}$ torr. A Finnigan LCQ ion trap mass spectrom e ter (Finnigan MAT; San Joes, CA, USA) equipped with an electrospray ion iza tion source was used for anal y sis of

Table 1. Chemical Name and Trade Name

No.	Trade name	MW	Chemical name
1	Iragnox 245	586	Tri(ehtyl glycol)bis-3-(3-*t*-buty-4-hydroxy-5-methylpheny)propionate
2	Iragnox 259	638	1,6-Hexamethylene bis-(3,5-di-*t*-butyl-4-hydroxyhydrocinnamate)
3	Iragnox 1010	1176	Pentaerythritol tetrakis[3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate]
4	Iragnox 1024	552	N,N-bis[1-oxo-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propane]hydrazine
5	Iragnox 1076	530	Octyldecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate
6	Iragnox 1098	636	N,N-hexamethylene bis(3,5-di-*t*-butyl-4-hydroxyhydrocinnamamide)
7	Iragnox 3114	783	Tris(3,5-di-*t*-butyl-4-hydroxybenzyl)isocyanurate
8	Naugard 524	646	Tris(2,4-dk-*t*-butylphenyl)phosphite
9	Tinuvin P	225	2-(2-hydroxy-5-methylphenyl)-2H-benzotriazole
10	Tinuvin 144	684	2-*t*-Butyl-2-(4-hydroxy-3,5-di-*t*-butylbenzyl)[bis(methy-2,2,6,6-tetramethyl-4-piperidinyl)]dipropionate
11	Tinuvin 320	323	2-(2-Hydroxy-3,5-di-*t*-butylpheny)-2H-benzotriazole
12	Tinuvin 326	315	2-(3-*t*-Butyl-2-hydroxy-5-methylphenyl)-2H-5-chlorbenzotriazole
13	Tinuvin 328	351	2-(2-Hydroxy-3,5-di-*t*-amylphenyl)-2H-benzotriazole
14	Tinuvin 440	435	8-Acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro(4,5)decane-2,4-dione
15	Tinuvin 770	480	Bis(2,2,6,6-tetramethyl-4-piperidinyl)sebacate
16	Tinuvin 622	≥ 3000	Poly-(N-b-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxy-piperdiyl succinate)
17	Chimassorb 994	≤ 2500	Poly-{6-[1,1,3,3-tetramethylbutyl]-imino]-1,3,5-triaine-2,4-diyl}{2-(2,2,6,6,-tetramethylpiperinyl)-imino}

high molecular weight additives and the low energy CID experiments.

RESULTS AND DISCUSSION

MALDI mass spectra of polymer additives

In MALDI, sample is embedded in a low molecular weight matrix that enhances sample ionization. Strong absorbance at the wave length and good co-crystallization with sample are critical for ionization efficiency. Therefore, the success of this technique largely depends on the choice of the matrix. Different matrices, such as dithranol, ferrulic acid and 2,5-dihydroxybenzoic acids (2,5-DHB), have been used in the analysis of various synthetic polymers.[26-28] These matrices were studied and the results showed that 2,5-DHB pro-

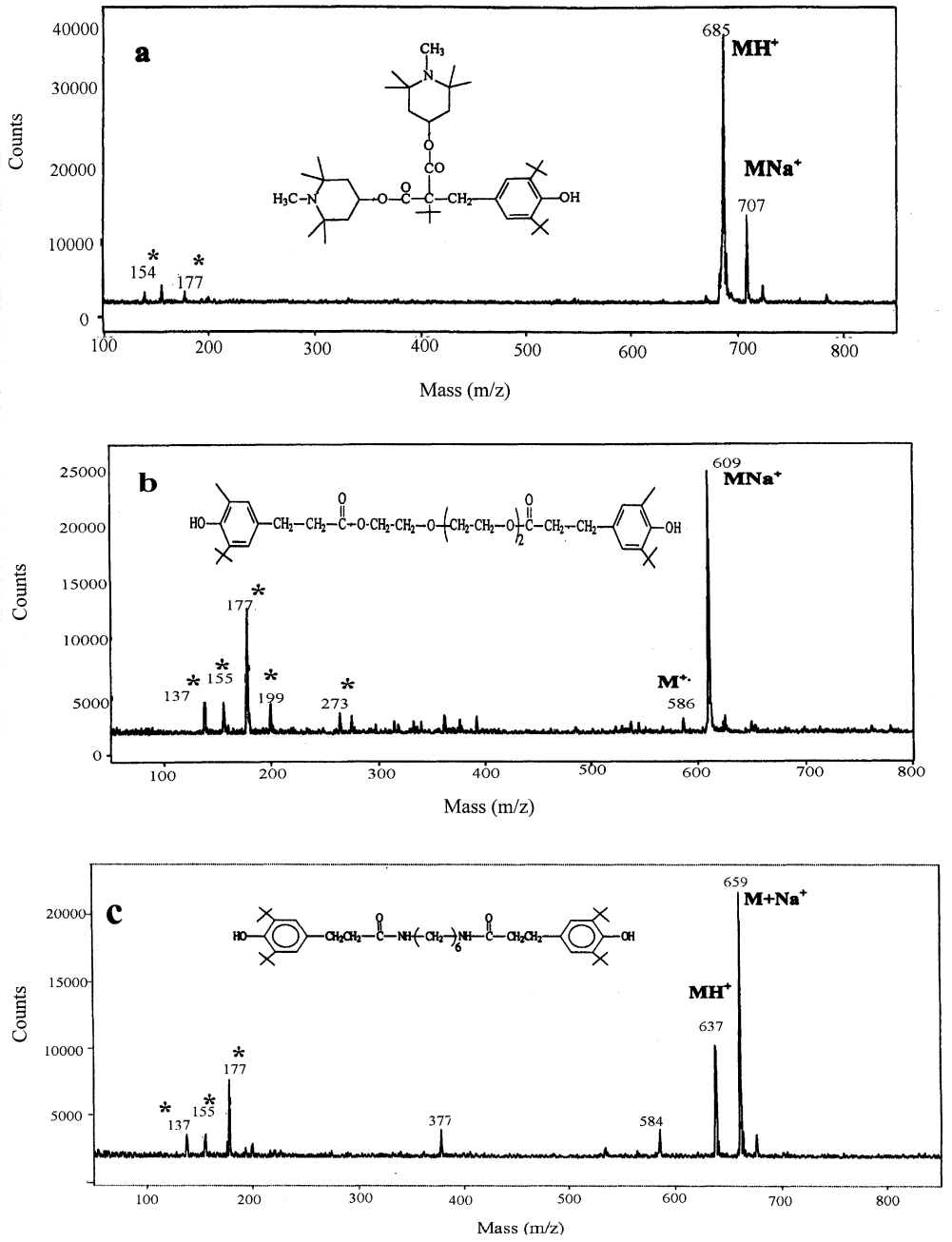

Fig. 1. (a) The MALDI mass spectrum of Tinuvin 144. (b) The MALDI mass spectrum of Irganox 245. (c) The MALDI mass spectrum of Irganox 1098 (*: matrix ion).

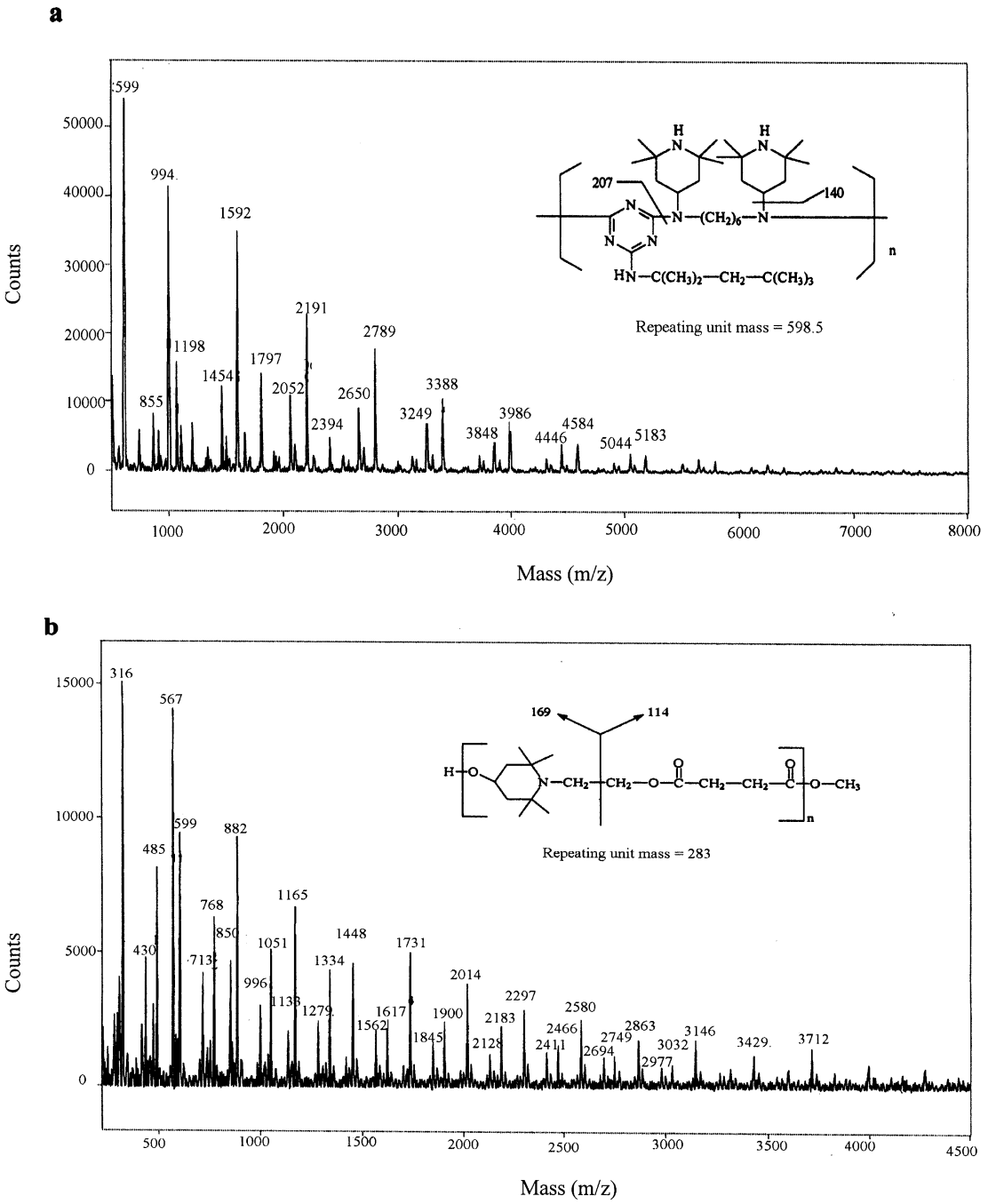

Fig. 2. The MALDI mass spec trum of (a) Chimassorb 944 (b) Tinuvin 622.

vided the most in tense analyte sig nals and the least abun dant ma trix ions. The pro duc tion of few ma trix ions would make the iden ti fi ca tion of ad di tives eas ier. Ac cord ingly, 2,5-DHB was used as the ma trix through out the study.

Con tin u ous as well as de layed ex trac tions were stud ied for the anal y sis of poly mer ad di tives. The re sults showed that there was less frag men ta tion in de layed ex trac tion. This is most likely due to the fact that the col li sion be tween the analyte ion and ma trix mol e cules is re duced greatly be cause of the de lay time. In the anal y sis of mix tures, such as the anal y sis of ad di tives in poly mer ex tract, it is eas ier to iden tify the ad di tives if there is less frag ment ions in the mass spec trum.

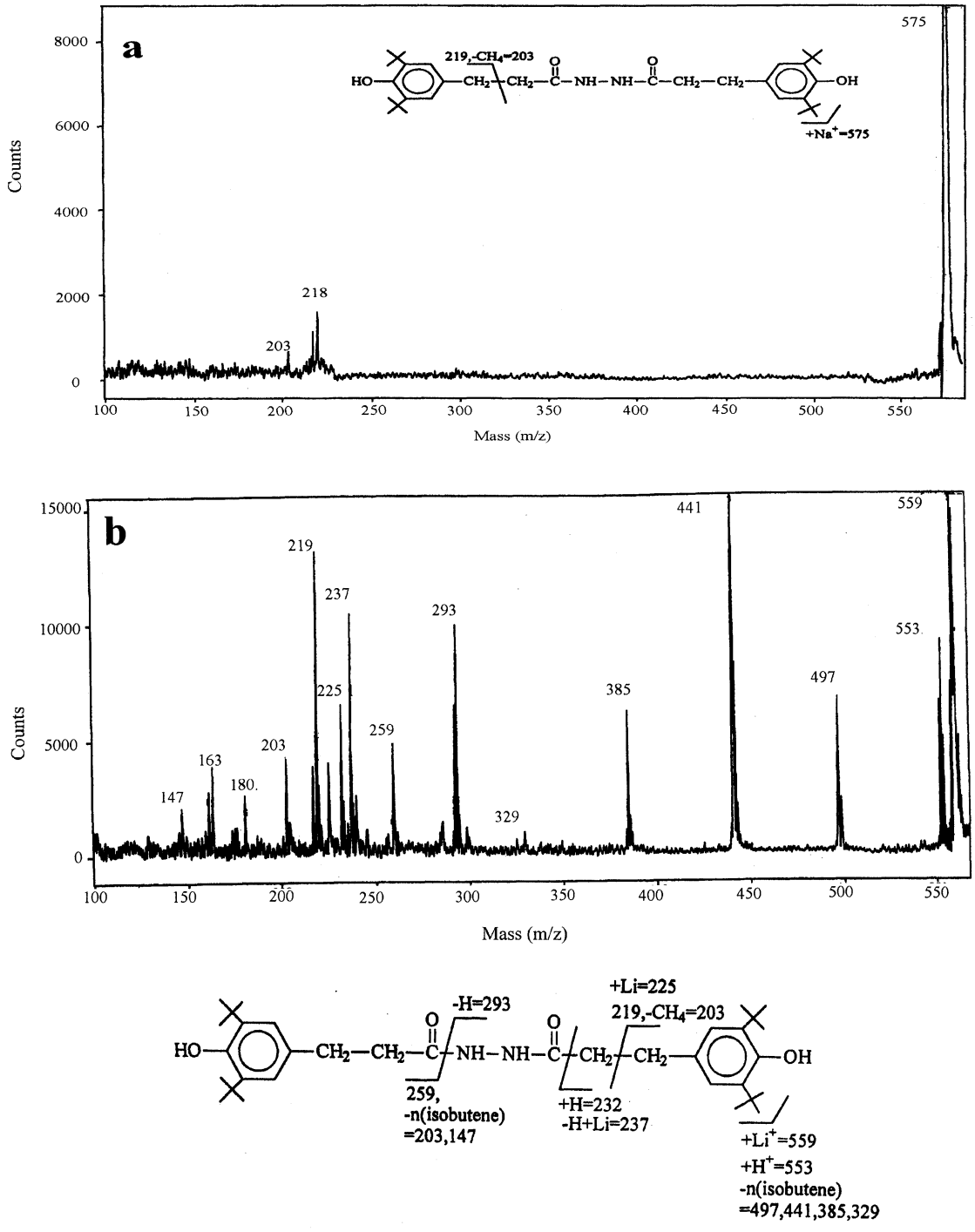

Fig. 3. The CID mass spec trum of (a) $[M+Na]^+$ ion (b) $[M+Li]^+$ ion of Irganox 1024.

There fore, de layed ex trac tion would make a better choice than con tin u ous ex trac tion. An other ad van tage of us ing de-layed ex trac tion is that the res o lu tion is also higher than that of con tin u ous ex trac tion.

Ad di tives listed in Ta ble 1 were an a lyzed by MALDI. Typ i cal MALDI mass spec tra of poly mer ad di tives are shown in Fig. 1. The mass spec tra of Tinuvin UV sta bi liz ers were char ac ter ized with $[M+H]^+$ or $[M+H]^+/[M+Na]^+$ ion with es-

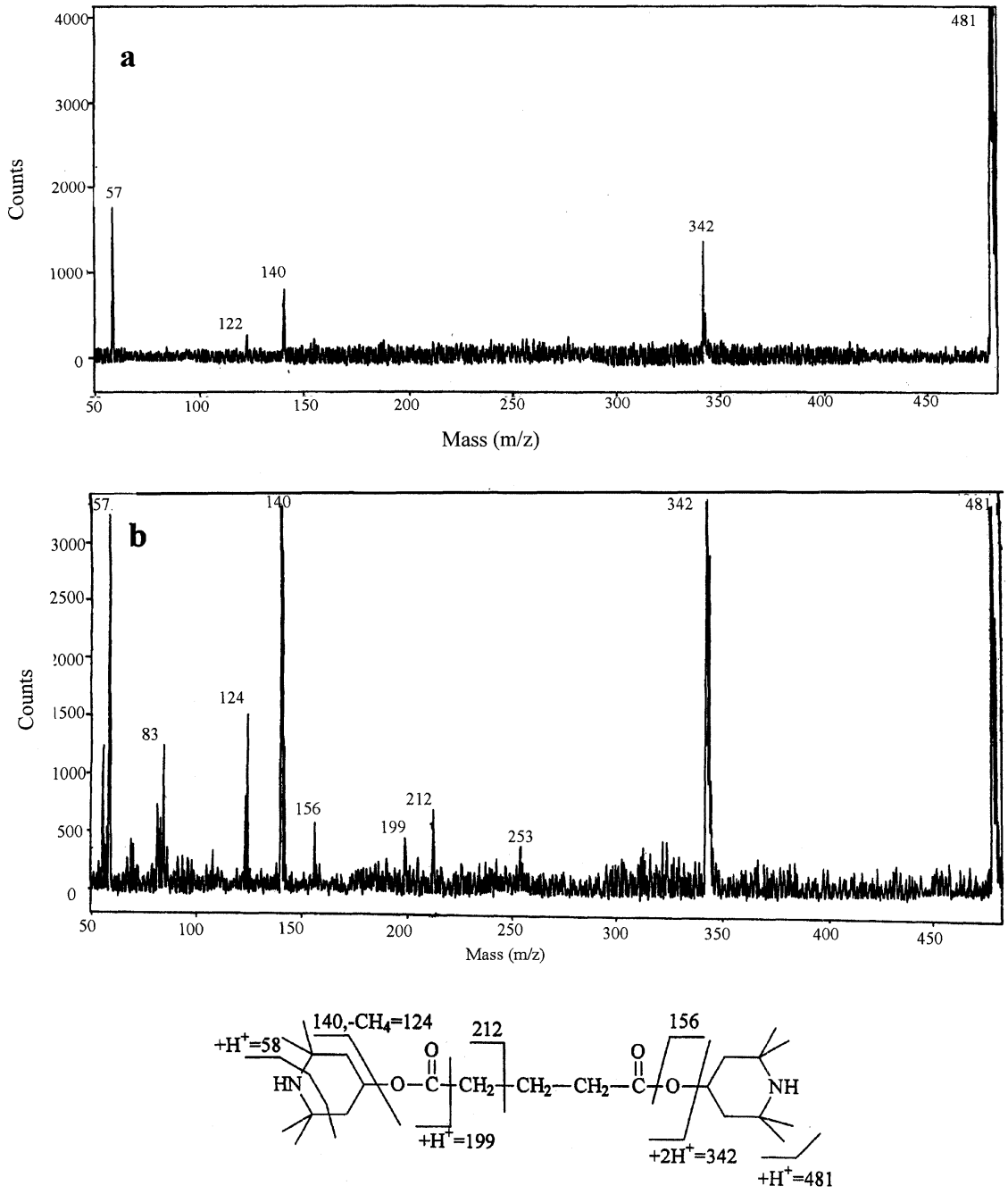

Fig. 4. (a) The PSD mass spectrum of Tinuvin 770 with continuous extraction. (b) The CID mass spectrum of Tinuvin 770 with delayed extraction.

sentially no fragmentation (Fig. 1a). Irganox antioxidants were characterized with $[M^{+\bullet}]/[M+Na]^+$ (Fig. 1b) or $[M+H]^+/[M+Na]^+$ ions (Fig. 1c) depending on the basicity of the molecules.

To reduce the loss during processing and services, there is an increase in the use of high molecular weight additives. We have analyzed several high molecular weight additives by FAB, DCI, APCI, ESI and none of these techniques was capable of providing good quality mass spectrum. Because of its superb capability in the analysis of very large molecules, MALDI is expected to provide a better alternative to the analysis of these additives. The MALDI mass spectra of two high

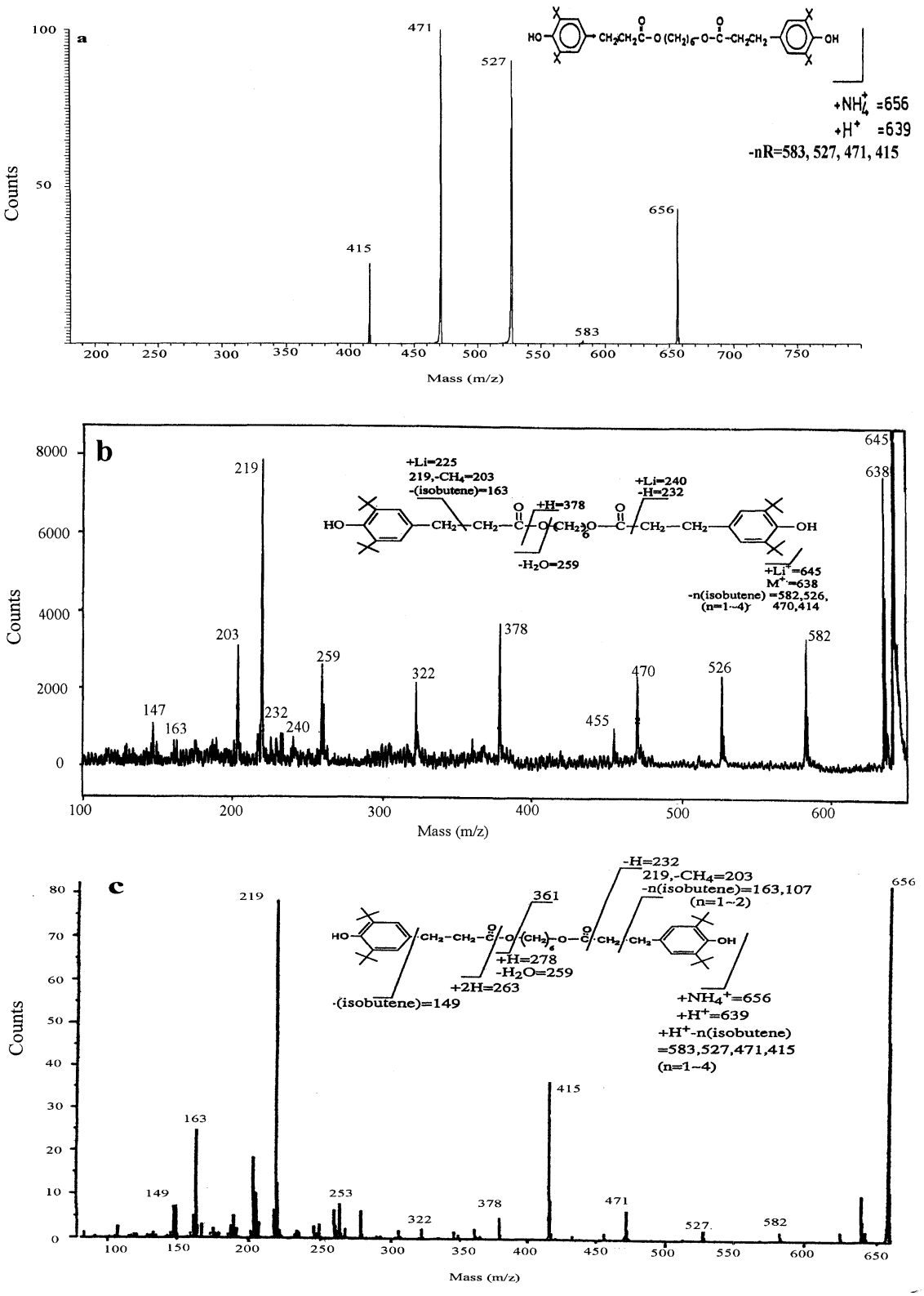

Fig. 5. (a) The CID mass spec trum of Irganox 259 $[M+NH_4]^+$ ac quired with an ion trap mass spec trom e ter. (b) The CID mass spec trum of Irganox 259 $[M+Li]^+$ ac quired with a MALDI TOF mass spec trom e ter. (c) The CID mass spectrum of Irganox 259 $[M+NH_4]^+$ ac quired with a sec tor in stru ment.

Table 2. The Product Ions of Polymer Additives

	Trade name (Formula)	Product ion
1	Irganox 245 $C_{34}H_{50}O_8$	530, 474, 368, 263, 198, 190, 177, 161
2	Irganox 259 $C_{40}H_{62}O_6$	582, 526, 470, 378, 322, 259, 219, 203
3	Irganox 1010 $C_{73}H_{108}O_{12}$	1120, 1064, 1009, 952, 899, 259, 219, 203
4	Irganox 1024 $C_{34}H_{52}N_2O_4$	497, 441, 385, 293, 259, 232, 237, 219, 203
5	Irganox 1076 $C_{35}H_{62}O_3$	515, 475, 259, 232, 219, 203
6	Irganox 1098 $C_{40}H_{64}N_2O_4$	581, 525, 469, 377, 321, 259, 219, 203, 163
7	Irganox 3114 $C_{48}H_{69}N_3O_6$	565, 436, 354, 346, 260, 219, 203, 163
8	Oxidized Naguard 524 $C_{42}H_{63}O_4P$	607, 551, 495, 459, 403
9	Tinuvin P $C_{13}H_{11}N_3O$	120, 107, 92
10	Tinuvin 144 $C_{42}H_{72}N_2O_5$	532, 219, 154, 138, 123, 72
11	Tinuvin 320 $C_{20}H_{25}N_3O$	308, 268, 212, 57
12	Tinuvin 326 $C_{17}H_{18}ClN_3O$	300, 260, 57
13	Tinuvin 328 $C_{22}H_{29}N_3O$	336, 322, 282, 71
14	Tinuvin 440 $C_{25}H_{45}N_3O_3$	418, 394, 377, 321, 110, 100, 58
15	Tinuvin 770 $C_{28}H_{52}N_2O_4$	342, 212, 199, 140, 124, 58

mo lec u lar weight ad di tives, Chimassorb 944 and Tinuvin 622, are shown in Fig. 2. In ad di tion to the ions (*m/z* = 599, 1198, 1797) re lated to the in tact mol e cules (re peat ing unit mass = 598 Da.), two ma jor se ries of ions were also ob served. The ions at *m/z* 994, 1592, 2191, 2789, 3388, 3986, 4585, 5183 cor re sponds to the loss of one triazine group from the oli go mers. The ions at *m/z* 1454, 2052, 2650, 3249, 3848, 4446, and 5044 cor re sponds to the loss of one piperidyl group from the pre vi ous se ries. Tinuvin 622 sta bi lizer showed three ma jor se ries of ions (Fig. 2b). The ions at *m/z* 316, 599, 882, 1165, 1448, 1731, 2014, 2297, 2580, 2863, 3146, 3429, and 3712 cor re sponds to the in tact oli go mers with re peat ing mass of 283 amu. The ions at *m/z* 485, 768, 1051, 1334, 1617, and 1900 cor re spond to the loss of a diester end group from the oli go mers. The ions at *m/z* 713, 996, 1279, 1562, 1845 cor re-spond to the loss of a piperidyl group from the lin ear oli go-mers.

MS/MS of polymer additives

The pseudomolecular ions in MALDI mass spec tra pro-vide ten ta tive as sign ment of the ad di tives pres ent in poly mer ex tracts. MS/MS of these pseudomolecular ions would pro-vide much higher con fi dence in ad di tive as sign ment. The study of ad di tives by MS/MS in di cated that, in com par i son with $[M+H]^+$, it was rather dif fi cult to frag ment $[M+Na]^+$ ion (Fig. 3a). For many Irganox ad di tives, $[M+Na]^+$ is ei ther the only one or the ma jor pseudomolecular ion, thus, it is dif fi cult to ob tain a use ful prod uct ion spec trum. It has re cently been shown that lith ium adduct frag ments more ex ten sively than so dium adduct.[28] There fore, lith ium salt was added to the ma-trix to pro mote the for ma tion of $[M+Li]^+$ ion. As ex pected, many more fragments were observed in the CID of the $[M+Li]^+$ ion (Fig. 3b).

In our MALDI-TOF in stru ment, PSD and CID are the two means to ac quire MS/MS spec tra. Metastable de com po-si tion dur ing the flight through a MALDI-TOF in stru ment is re ferred to post-source de cay. The re sult ing frag ment ions pos sess dif fer ent ki netic en er gies and there fore can be an a-lyzed by step wise de creas ing the po ten tial of the re flec tor. Al though in some ad di tives, such as Tinuvin 326, 328 and 440, the PSD spec tra were es sen tially the same as the CID spec tra; gen er ally, CID pro duced more frag ment ions than PSD as shown in Fig. 4. Ac cord ingly, CID was used in the anal y sis of ad di tives in poly mer ex tract.

In the in creas ing of in ter nal en ergy with CID, the ac cel-er a tion volt age of the mass spec trom e ter plays an im por tant role be cause the max i mum en ergy, which can be con verted into in ter nal en ergy, is pro por tional to the translational en-ergy of the pre cur sor ion. The prod uct ion spec tra, ob tained from three dif fer ent in stru ments, of an an ti ox i dant-Irganox 259 are shown in Fig. 5. As can be seen, many more prod uct ions were de tected in high-energy in stru ments (Fig. 5b, 5c) than in the low en ergy in stru ment (Fig. 5a). The CID spec tra ob tained from MALDI-TOF (for ex am ple, Fig. 5b) are sim i-lar but not quite the same as the spec tra ob tained from a sec tor in stru ment (for ex am ple, Fig. 5c). One pos si ble rea son is that the ac cel er a tion volt age of the TOF in stru ment (20 kV) is higher than that of the sec tor in stru ment (10 kV). An other pos si ble ex pla na tion is the dif fer ence in the frag men ta tion pat tern of $[M+Li]^+$ and $[M+H]^+$ ions. The ma jor frag ment ions of var i ous UV-stabilizers and an ti ox i dants are listed in Ta ble 2.

The analysis of additives in polyethylene

The ad di tives in polyethylenes were ex tracted with the pro ce dures used in ear lier DCI anal y sis[14] and an a lyzed di-rectly by MALDI. The MALDI mass spec trum of one sam ple

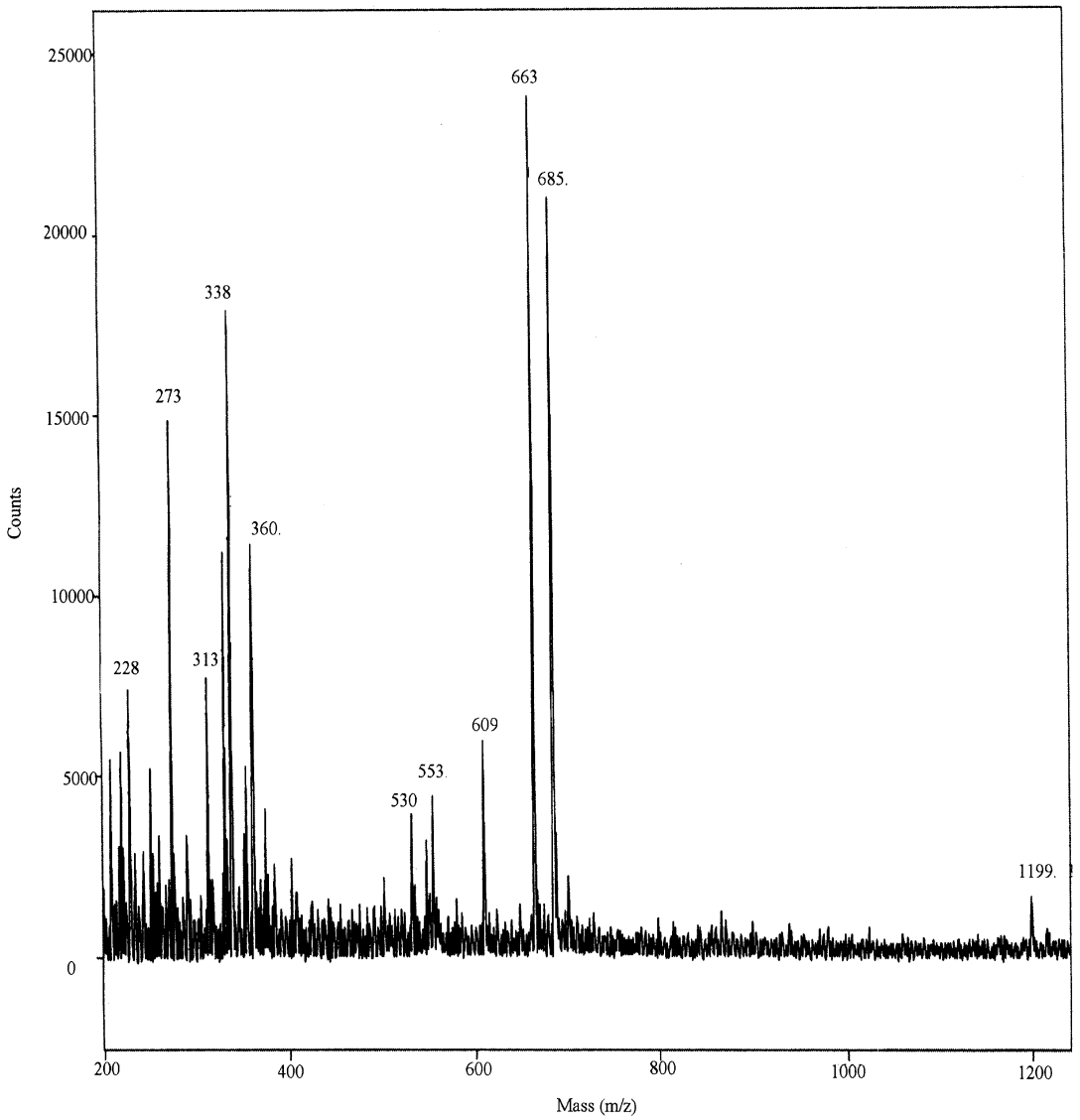

Fig. 6. MALDI mass spec trum of a poly eth yl ene ex tract.

ex tract is shown in Fig. 6. Ex cept the *m/z* 609 ion, the ma jor ions at *m/z* = 338/360, 530/553, 663/685, and 1199 are ten ta-tively as signed as $[M+H]^+/[M+Na]^+$ of Erucamide, $[M]^+/[M+Na]^+$ of Irganox 1076, $[M+H]^+/[M+Na]^+$ of ox i dized Naugard 524 and $[M+Na]^+$ of Irganox 1010 re spec tively. In com par i son with the anal y sis of ad di tive stan dards, the spec-trum of the ex tract was not very re pro duc ible and only a few spots could pro duce the spec trum. One pos si ble cause is that the low mo lec u lar weight poly eth yl ene mol e cules are not precipitated completely when the low molecular weight polyethylenes in to lu ene are pre cip i tated with meth a nol. Crys tal li za tion is be lieved to be crit i cal for the qual ity of the MALDI spec trum and the ex is tence of many low mo lec u lar weight polyethylenes in the ex tract may in ter fere the pro cess of crys tal li za tion. This prob lem was par tially over come with the use of ac e tone in stead of meth a nol to pre cip i tate the polyethylenes. The sig nals were found to be more re pro duc-ible if ac e tone was used in the pre cip i ta tion of low mo lec u lar weight polyethylenes.

To im prove the con fi dence of com pound as sign ment, the pseudomolecular ions of the ex tract were sub jected to CID anal y sis. Based on the CID spec tra, the *m/z* = 663, 685 ions was as signed as the $[M+H]^+/[M+Na]^+$ ion of ox i dized Naguard 524. The ion at *m/z* = 338, 360 was con firmed as the am ide wax Erucamide. (Fig. 7) The sig nals at 530/553 and 1199 were too weak to pro duce a use ful prod uct ion spec-

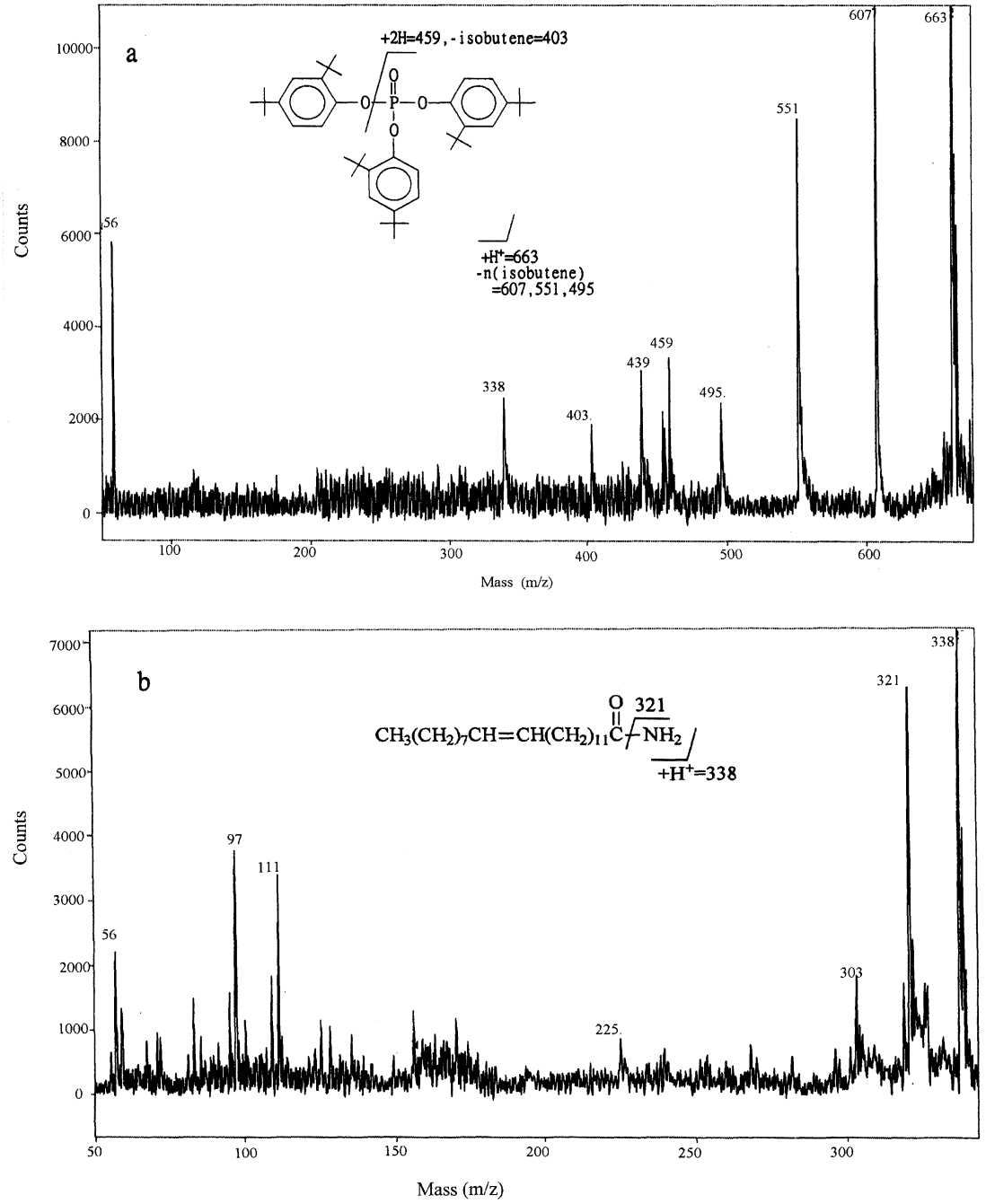

Fig. 7. The CID mass spec trum of (a) *m/z* = 663 ion and (b) *m/z* = 338 ion from the poly mer ex tract.

trum.

CONCLUSION

MALDI was found to be a use ful method for the iden ti-fi ca tion of poly mer ad di tives in poly eth yl ene. With the in-strument operated under delayed extraction and using 2,5-dihydroxybenzoic acid (2,5-DHB) as the ma trix, in gen-eral, only pseudomolecular ions were ob served. Be cause of the ob ser va tion of only pseudomolecular ions, ten ta tive as-sign ment can be eas ily made in the anal y sis of ad di tives in

polymer extract. To confirm the tentative assignment, CID provides more information than PSD. While MALDI was found to be superior to other ionization techniques in the analysis of high molecular weight additives, sample preparation in MALDI was more critical in the analysis of real samples. Currently, we are looking for methods to separate the low molecular weight polyethylene molecules before the MALDI analysis.

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Key Words

Polyethylene; MALDI-TOF; Polymer additives; Collision induced dissociation (CID); Mass spectrometer.

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