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Emerging Mass Spectrometric Tools for Analysis of Polymers and Polymer Additives

Nina Aminlashgari and Minna Hakkarainen

Abstract The field of mass spectrometry has experienced enormous developments in the last few years. New interesting mass spectrometric techniques have arrived and there have been further developments in the existing methods that have opened up new possibilities for the analysis of increasingly complex polymer structures and compositions. Some of the most interesting emerging techniques for polymer analysis are briefly reviewed in this paper. These include new developments in laser desorption ionization techniques, like solvent-free matrix-assisted laser desorption ionization (solvent-free MALDI) and surface-assisted laser desorption ionization (SALDI) mass spectrometry, and the developments in secondary ion mass spectrometry (SIMS), such as gentle-SIMS and cluster SIMS. Desorption electrospray ionization (DESI) mass spectrometry and direct analysis in real time (DART) mass spectrometry offer great possibilities for analysis of solid samples in their native form, while mobility separation prior to mass spectrometric analysis in ion mobility spectrometry (IMS) mass spectrometry further facilitates the analysis of complex polymer structures. The potential of these new developments is still largely unexplored, but they will surely further strengthen the position of mass spectrometry as an irreplaceable tool for polymer characterization.

Keywords Additives · Degradation products · Desorption ionization mass spectrometry · Laser desorption ionization mass spectrometry · Mass spectrometry · Polymer analysis · Secondary ion mass spectrometry

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Abbreviations

APCI	Atmospheric pressure chemical ionization
APPI	Atmospheric pressure photoionization
BFRs	Brominated flame retardants
CHCA	α-Cyano-4-hydroxycinnamic acid
CID	Collision-induced dissociation
CNTs	Carbon nanotubes
DART	Direct analysis in real time
DBP	Dibutyl phthalate
DEHP	Di-2-ethylhexyl phthalate
DESI	Desorption electrospray ionization
DHB	2,5-Dihydroxybenzonic acid
DIDP	Diisodecyl phthalate
DINP	Diisononyl phthalate
DIOS	Desorption ionization on porous silicon
DNOP	Di-*n*-octyl phthalate
ECD	Electron-capture dissociation
ERM	European Reference Material
ESI-MS	Electrospray ionization-mass spectrometry
FTICR-MS	Fourier transform ion cyclotron resonance- mass spectrometry
FTMS	Fourier transform mass spectrometry
GC-MS	Gas chromatography–mass spectrometry
HDPE	High density polyethylene

HPLC-UV	High performance liquid chromatography–ultraviolet
ICP-MS	Inductive coupled plasma–mass spectrometry
IMS-MS	Ion mobility spectrometry–mass spectrometry
LC	Liquid chromatography
LDI-MS	Laser desorption ionization–mass spectrometry
LOD	Limits of detection
m/*z*	Mass-to-charge ratio
MALDI-MS	Matrix-assisted laser desorption ionization–mass spectrometry
MS	Mass spectrometry
MS/MS	Tandem mass spectrometry
NaI	Sodium iodide
PAE	Phthalic acid esters
PALDI-MS	Polymer-assisted laser desorption ionization–mass spectrometry
PAM	Polyacrylamide
PBBs	Polybrominated biphenyls
PBDEs	Polybrominated diphenyl ethers
PDMS	Poly(dimethyl siloxane)
PEG	Poly(ethylene glycol)
PET	Poly(ethylene terephthalate)
PGS	Pyrolytic highly oriented graphite polymer film
PLA	Polylactide
PMMA	Polymethylmethacrylate
PMS	Poly(α-methyl styrene)
PP	Polypropylene
ppb	Parts per billion
PPEs	Polyphosphoesters
PPG	Poly(propylene glycol)
PS	Polystyrene
PTMG	Poly(tetramethylene glycol)
PVC	Polyvinyl chloride
S/N	Signal-to-noise ratio
SALDI-MS	Surface-assisted laser desorption ionization-mass spectrometry
SIMS	Secondary ion mass spectrometry
TFA	Trifluoroacetic acid
TOF	Time-of-flight
VOCs	Volatile organic compounds

1 Introduction

Soft ionization mass spectrometric techniques have become dominant tools for analysis of polymers and polymer additives. Matrix-assisted laser desorption ionization–mass spectrometry (MALDI-MS) together with electrospray ionization–mass spectrometry (ESI-MS) have been two preeminent techniques for the analysis of higher molecular mass synthetic compounds. The difficulty with ESI-MS is the multiply charged ion adducts when dealing with polymers with high molar mass distribution. Industrial polymeric materials contain several low molecular weight compounds, i.e., additives to enhance properties such as durability, thermo-oxidative stability, or processability. The drawback with MALDI is the difficulty in studying these low molecular weight compounds. The matrix applied in MALDI interferes with the low mass range and often makes it impossible to detect low molecular weight compounds. Two approaches have been to use high molecular weight matrices or to pick a matrix that does not interfere with the analyte signal [1].

The analysis of low molecular weight compounds in polymers is important for many applications to ensure the safe use of plastic products. For example, in the food industry, the quality, environmental, and health controls are important and are followed by agencies such as the US Food and Drug Administration. Moreover, the US Environmental Protection Agency is concerned with the presence of compounds such as bisphenol A and brominated flame retardants (BFRs) in the plastic materials. Different extraction methods combined with gas chromatography–mass spectrometry (GC-MS) and liquid chromatography–mass spectrometry (LC-MS) have been employed with excellent results in many studies of low molecular weight compounds such as additives and polymer degradation products. However, these techniques are often time-consuming because of long sample preparation steps prior to analysis and they have limitations concerning the volatility, solubility, or thermal stability of the analytes.

In order to overcome all these problems, a new generation of mass spectrometric techniques has been developed for analysis of small molecules. This chapter will introduce emerging mass spectrometric tools that do not need a matrix, such as desorption ionization on porous silicon (DIOS) and surface-assisted laser desorption ionization–mass spectrometry (SALDI-MS). The similarity of these two techniques is that they use a surface instead of a matrix as a target for the analysis. Another approach in mass spectrometry has been the direct analysis of solid, liquid, and gas samples with new ambient techniques. These techniques, including direct analysis in real time (DART) and desorption electrospray ionization (DESI), will be further described in Sect. 3. These ambient techniques have especially facilitated the sample preparation step as, in most cases, no sample preparation is needed at all. The possibility of analyzing samples in their untreated, native form introduces a new level of analysis in mass spectrometry.

In this chapter, alternative emerging techniques for mass spectrometric analysis of polymer and polymer additives are introduced and discussed. For instance, another important tool that often contributes to limitations in mass spectrometric analysis is the mass analyzer. Fourier transform ion cyclotron resonance–mass spectrometry (FTICR-MS) provides higher resolving power and higher mass accuracy. Ion mobility spectrometry–mass spectrometry (IMS-MS) on the other hand introduces mobility separation before mass spectrometric analysis, which enhances the possibility of performing structural analysis of complex polymeric materials. In addition, inductive coupled plasma–mass spectrometry (ICP-MS) is a technique that has been used for screening of heavy metal elements or BFRs in polymeric materials.

2 Laser Desorption Ionization Techniques

MALDI-MS is a routine tool for analysis of high molecular mass compounds such as synthetic polymers and biopolymers. Until now it has not been widely applied for the analysis of low molecular mass compounds. However, there has been increased interest in matrix-free methods for laser desorption ionization–mass spectrometry (LDI-MS) during the past decade to enable analysis of low molecular mass compounds. The main reason for this development is the difficulty in analyzing low molecular mass compounds ($<1{,}000$ m/z) with the traditional MALDI-MS due to matrix cluster ions that tend to interfere with the low mass range of the spectrum. These matrix limitations have led to the introduction of several LDI techniques for the analysis of small molecules.

2.1 Desorption Ionization on Silicon

Siuzdak and coworkers [2] developed one of the first LDI technique without matrix assistance, called DIOS. The porous silicon target is produced by etching silicon wafers to form a nanostructure surface, an effective semiconductive platform for desorption/ionization. The preparation of a DIOS plate is very important since the shape and pore size can influence the efficiency of the LDI. An efficient surface should have high porosity and pore size in order to increase the surface area for energy transfer from the surface to the analyte molecules [3].

DIOS has been successfully applied for the analysis of low molecular mass polymers such as polyesters [4]. Polyesters are common synthetic polymers widely used in industry. Polyesters often have high polydispersity. The presence of low molecular mass components can affect the physical properties of the polyester and therefore it is important to identify these compounds. MALDI measurements with two different matrices, the traditional α-cyano-4-hydroxycinnamic acid (CHCA) and 10,15,20-tetrakis(pentafluorophenyl)porphyrin F20TPP, were compared with the DIOS mass spectrum. The DIOS mass spectrum of the polyester was easier to evaluate because of the absence of interfering matrix cluster ions (see Fig. 1). The signals at $m/z > 2{,}500$ in the DIOS mass spectrum are more abundant, indicating a smaller mass discrimination in DIOS than in MALDI. The calculation of the average molecular mass for synthetic polymers might, thus, be more accurate with DIOS than with MALDI. Polyethers are also well-known polymers used as lubricants, stabilizers, removers, antifoaming agents, and raw materials for polyurethanes. DIOS has also been successfully applied for the quantitative analysis of polyethers in the form of diol and triol mixtures of poly(propylene glycol) (PPG) [5] and poly(ethylene glycol) (PEG) [6, 7]. This technique also permits the identification of polymer degradation products from, for example, poly(ethylene terephthalate) (PET) [8].

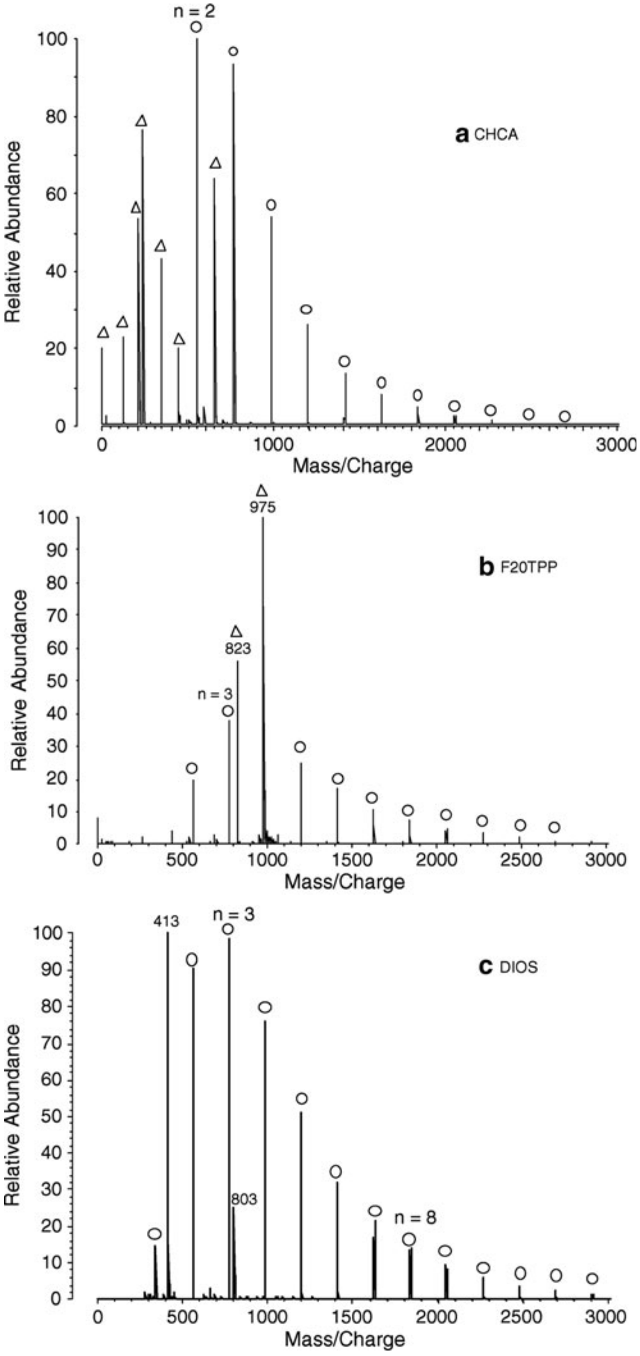

Fig. 1 Mass spectra of a low molecular mass polyester ($M_n = 600$) obtained by different methods: (**a**) MALDI spectrum with CHCA as matrix, (**b**) MALDI spectrum with F20TPP as matrix, and (**c**) DIOS using NaI as cationizing agent. The *circles* and *triangles* represent polyester ions and matrix-related ions respectively. Reprinted from [4] with permission of John Wiley and Sons. Copyright John Wiley and Sons (2004)

2.2 *Surface-Assisted Laser Desorption Ionization–Mass Spectrometry*

SALDI was originally developed by Tanaka et al. [9] who used cobalt nanoparticles in glycerol to analyze lysozyme and synthetic polymers. However, the method was first named by Sunner et al. [10] who used graphite powder as a matrix. The principal concept of the technique is a solid surface where analytes are deposited and ionized from. The traditional organic matrices in MALDI were replaced with a surface that is tailored to absorb the laser energy and transfer it to the analyte molecules in order to desorb them. The sensitivity and molecular weight distribution of SALDI is comparable with MALDI mass spectra [11]. The solid surfaces used in SALDI are not ionized, which makes it a good technique for analysis of small molecules. The physical and chemical properties of the applied surface have an important role in the desorption and ionization processes and it was soon concluded that carbon was a unique material and that surface roughness was essential. One of the most important features with SALDI is that, in contrast to MALDI, no interference of surface cluster ions is observed in the low mass region, which makes it easier to detect low molecular weight compounds (50–500 *m*/*z*).

2.2.1 SALDI Surfaces

Since the development of SALDI a number of materials have been studied for their function as surfaces, ranging from nano- to macroscaled materials. The majority of SALDI substrates can be divided into three different groups: carbon-based materials, silicon-based materials, and metal particle-based substrates. Inorganic nanoparticles have been utilized a lot because they offer a high surface area, simple sample preparation, and flexible deposit of samples under different conditions. The type, form, and size (micro- or nanosized particles) of the SALDI substrates have an important impact on the analytical performance. Among suitable SALDI surfaces are metals [12], metal oxides [13], carbon nanotubes [14], activated carbon [15], graphitized carbon black [16], silicon nitride nanoparticles [17], inorganic materials [18], surfactant-suppressed matrices [19], and some polymers such as poly(glycidyl methacrylate/divinylbenzene) [20].

Recently, gold and platinum metal nanoparticles were utilized as SALDI substrates for analysis of synthetic polymers [21]. Low molecular weight PEG (400, 1,000, 2,000, and 3,000 g mol^{-1}) and poly(methyl methacrylate) (PMMA) (1,890 g mol^{-1}) were analyzed with SALDI and the spectra compared with those from conventional MALDI using the organic matrix CHCA and 2,5-dihydroxybenzonic acid (DHB). It could be observed that gold and platinum nanoparticles yielded a better spectrum with almost no noise in the low mass range. In contrast, the quality of the spectrum obtained with CHCA was not as good. Additionally, it was confirmed that the particle size of the nanoparticles could affect the peak intensities in the mass spectrum. The peak shapes obtained after using platinum nanoparticles as surfaces or CHCA as an organic matrix are quite similar, whereas the peak shapes for PEG 400 g mol^{-1} analyzed on gold nanoparticle surfaces are more intensive in the low mass range. PMMA was also analyzed on gold nanoparticles and by using a traditional DHB matrix. The same trend was seen, i.e., the intensities of the SALDI spectrum are higher compared to the MALDI spectrum. This phenomena of higher signal intensity of the analytes in the low mass region was in agreement with an earlier study by Hillenkamp [22]. Here, it is interesting to consider the polymer–surface interactions that tend to be weak. However, polymers with higher molecular weight are not easily detached from a surface because there are more binding sites. Therefore, a higher energy may be necessary for the LDI process for higher molecular weight compounds, resulting in a mass spectrum containing a lot of fragmentation.

SALDI-MS with titanium dioxide nanoparticles (TiO_2), MALDI-MS, and DIOS-MS were examined as possible methods for analysis of the antioxidant Irganox 1010 in polypropylene (PP) materials [23]. TiO_2 nanoparticles were suspended with 2-propanol to a concentration of 0.33 wt%. Comparison of the mass spectra of standard solutions consisting of the internal standard Irganox 1098 and the analyte Irganox 1010 obtained by using the three different method showed that the background noise, below 500 *m*/*z*, is much higher for the MALDI- and DIOS-MS than for SALDI-MS. However, the ion intensity of Irganox 1098 after SALDI-MS was less sensitive compared to Irganox 1010. Additionally, quantitative analysis by the different techniques was also compared. For MALDI, the ionization efficiency was strongly dependent on the ratio of the analyte and matrix concentrations and therefore was not considered a suitable technique for quantitative analysis. Quantitative analysis by DIOS and SALDI could, however, be possible. Commercial and laboratory-produced PP materials were evaluated with SALDI-MS for quantitative analysis of antioxidants. The amount of Irganox 1010 in the PP samples was determined to be 0.51 wt% for the commercial and 0.48 wt% for the laboratory-produced PP compared to the actual content of 0.5 wt%. Irganox 1076 and calcium stearate were also added to the commercial PP but they were not detectable by the SALDI method used. The authors concluded that SALDI-MS with TiO_2 nanoparticles could be used for quantitative analysis of antioxidants within the range 0.01–2.00 wt% in PP.

Zinc oxide (ZnO) nanoparticles were evaluated for their potential to function as SALDI substrates for low molecular weight synthetic polymers of PPG 400 g mol^{-1} with aminopropyl ether endgroups, PEG 6,000 g mol^{-1}, polystyrene (PS) 2,400 g mol^{-1}, and PMMA 1,890 g mol^{-1} [11]. ZnO particles were suspended in methanol to achieve a concentration of 0.17–1.0 wt%. A MALDI mass spectrum with DHB as matrix and a SALDI mass spectrum with TiO_2 and ZnO nanoparticles of PEG 6,000 g mol^{-1} is shown in Fig. 2. The results from TiO_2-SALDI showed generated fragment ions and no ions at around 6,000 g mol^{-1}. TiO_2 is known to have strong UV photocatalytic activity and this could be the reason for the observed degradation of PEG. In contrast, the molecular weight distribution for ZnO-SALDI was comparable to MALDI with DHB, and no fragmentation was observed because the photocatalytic activity of ZnO is not strong enough. The number average

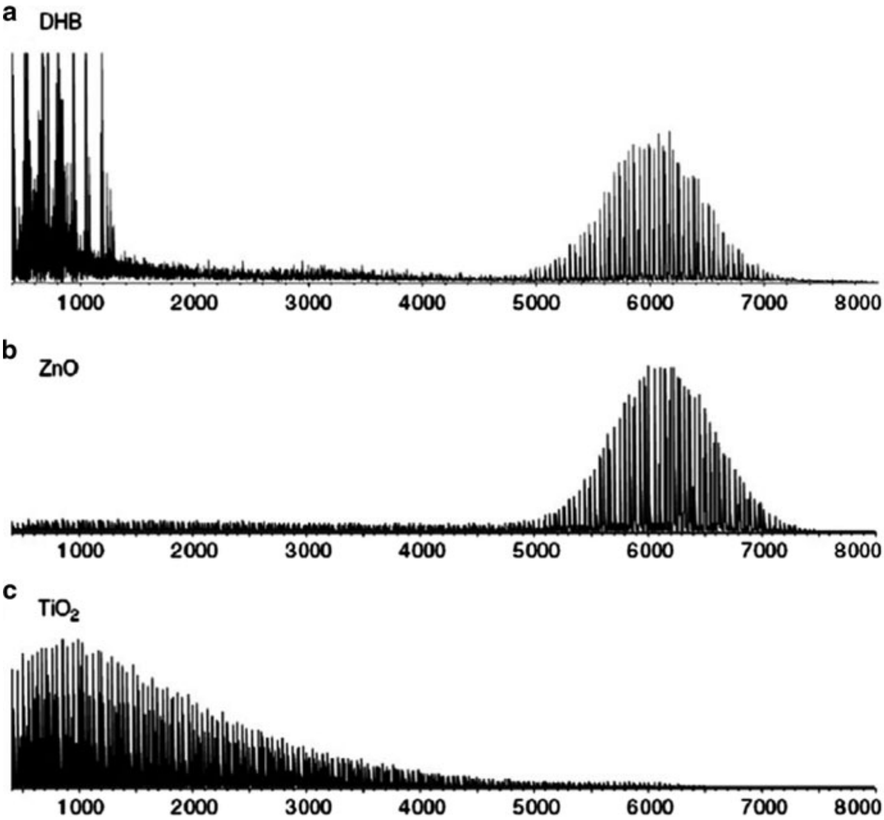

Fig. 2 LDI-MS of polyethylene glycol 6000 obtained with (**a**) DHB as a matrix, (**b**) ZnO nanoparticles as a surface, and (**c**) TiO_2 nanoparticles as a surface. Reprinted from [11] with permission of John Wiley and Sons. Copyright John Wiley and Sons (2008)

molecular weight (M_n) and the polydispersity index (PDI) was similar for SALDI and MALDI: for PS, $M_n = 2{,}380$ and PDI = 1.03 for ZnO, and $M_n = 2{,}245$ and PDI =1.04 for DHB; for PMMA, $M_n = 1{,}755$ and PDI = 1.09 for ZnO, and $M_n = 1{,}773$ and PDI = 1.10 for DHB. ZnO showed great potential as SALDI substrate for analysis of synthetic polymers. More studies are, however, needed to conclude whether it can be used as a more general matrix or if it is limited to the type of polymer. For example, it was also possible to obtain a mass spectrum for higher molecular weight PEG (10,000 g mol^{-1}) but not for PS (9,000 g mol^{-1}). In Fig. 3, the mass spectra for PS and PMMA obtained by ZnO-SALDI are shown.

Drawbacks with nanoparticles as SALDI substrates are possible instrument contamination and the difficulty in handling free nanoparticles. In a recent study, nanoparticles were immobilized into polylactide (PLA) and evaluated as SALDI substrates for detection of drugs for human use: propanolol, acebutolol, and carbamazepine [24]. Nanocomposite films were made of PLA blend mixed with eight

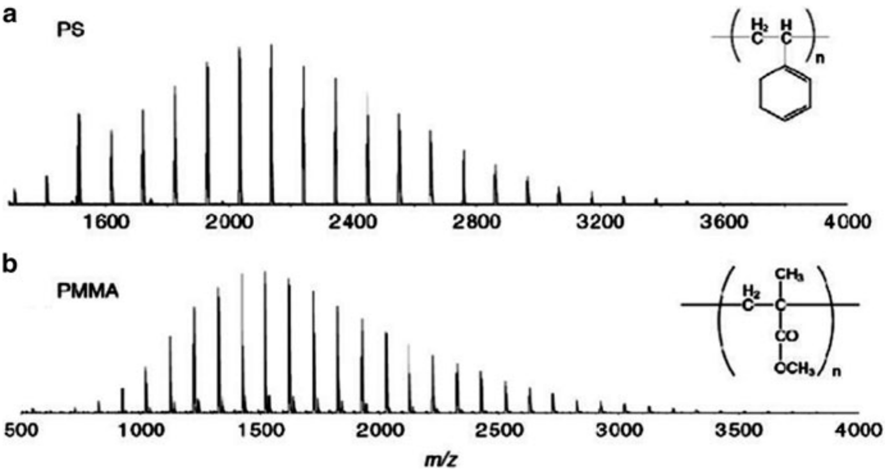

Fig. 3 ZnO-SALDI-MS spectra of (**a**) polystyrene and (**b**) polymethylmethacrylate. Reprinted from [11] with permission of John Wiley and Sons. Copyright John Wiley and Sons (2008)

different nanoparticles: TiO_2, magnesium oxide, silicon nitride, graphitized carbon black, silicon dioxide, halloysite nanoclay, montmorillonite nanoclay, and hydroxyapatite. The concentrations of nanoparticles in the polymer matrix were 5, 10, 20, and 30 wt%. These nanocomposites could provide a new strategy of easy-to-handle surfaces for rapid SALDI-MS analysis. The background noise of a blank nanocomposite spot was determined for all surfaces to see if the low mass range was clean, without any interference from surface cluster ions. The background spectrum corresponding to the PLA containing 10% TiO_2 is demonstrated in Fig. 4. A clean background is shown except for the peak at 64.1 *m*/*z*, which corresponds to the fragment TiO. Pure PLA surface was compared with surfaces containing nanoparticles and it was obvious that the contribution of nanoparticles affected the ionization/desorption process and a higher signal-to-noise (S/N) ratio was obtained after addition of nanoparticles. The percentage of nanoparticles could also affect the results and most surfaces containing 10 wt% nanoparticles gave better S/N values than the surfaces containing 30% nanoparticles. The spectrum of carbamazepine spotted on the PLA with 10 wt% TiO_2 is shown in Fig. 5. A certain amount of nanoparticles could enhance the S/N ratio. However, a larger amount of nanoparticles led to a lower S/N ratio, which could be to do with the hydrophobicity of the surface, as seen from the contact angle measurements. The analyte hydrophobicity was also considered; acebutolol was the least hydrophobic analyte and generally gave the highest S/N ratio. Propanolol was the most hydrophobic analyte and gave the lowest S/N ratios. The limits of detection (LOD) for all the surfaces were 1.7–56.3 ppm. However, the best surface was the one containing 10 wt% silicon nitride, giving relative standard deviations for the S/N values of 20–30%. In an earlier study, silicon nitride was used as pure nanoparticles and showed excellent results as a SALDI medium for analysis of drugs [17].

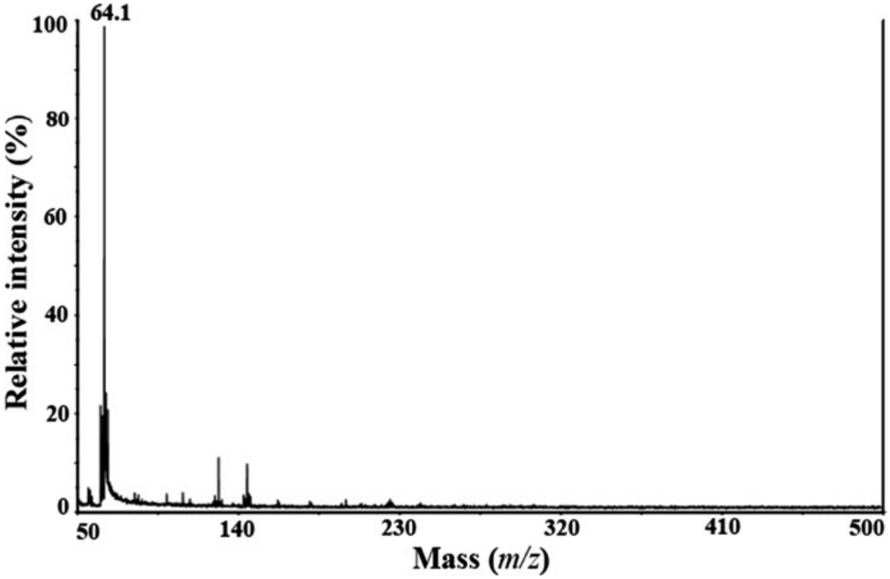

Fig. 4 SALDI-MS background spectrum of PLA surface containing 10% TiO_2. Reprinted from [24] with permission of The Royal Society of Chemistry. Copyright The Royal Society of Chemistry (2011)

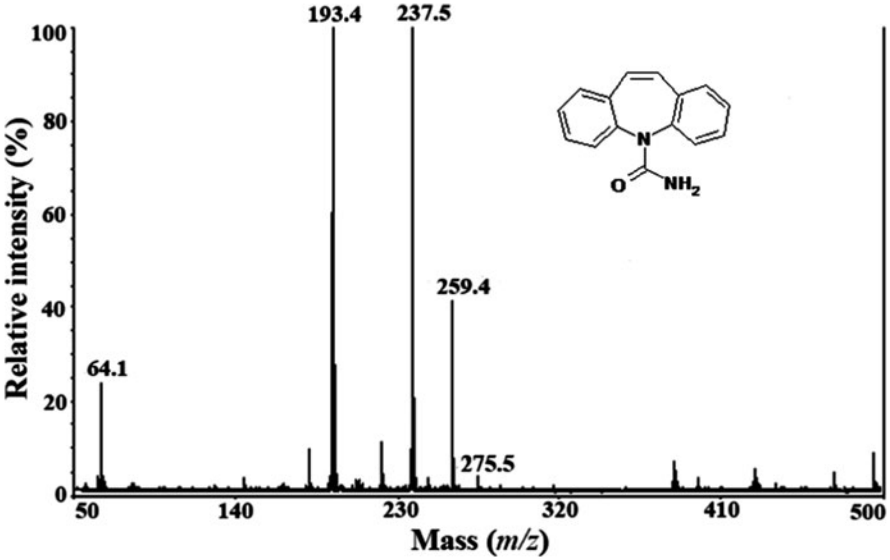

Fig. 5 SALDI-MS spectrum of carbamazepine on the surface of PLA containing 10% TiO_2. The proton adduct, sodium adduct, and potassium adduct together with a fragment ion is observed at *m*/*z* 237.5, 259.4, 275.5, and 193.4 respectively. Reprinted from [24] with permission of The Royal Society of Chemistry. Copyright The Royal Society of Chemistry (2011)

Polymer degradation products are typically analyzed with ESI-MS [25, 26] and GC-MS [27, 28], however, extraction methods are often necessary prior to analysis. Recently, SALDI-MS has shown great potential for analysis of polyester degradation products. Three different polycaprolactones (PCLs) with molecular weights of 900, 1,250, and 2,000 g mol^{-1} were employed for development of a SALDI-MS method for analysis of degradation products. The method development was carried out with different combinations of nanoparticles, solvents, and cationizing agents. Graphitizied carbon black, silicon nitride, TiO_2, halloysite nanoclay, and magnesium hydroxide were employed as potential surfaces. However, the most promising surfaces were halloysite nanoclay and magnesium hydroxide. Figure 6 shows the analysis of PCL 900 g mol^{-1} with magnesium hydroxide surface and either conventional trifluoroacetic acid (TFA) or sodium iodide (at two different concentrations). The spectra show the increased intensities using sodium iodide over the conventional TFA. In addition, compared to MALDI-MS, the resolution was better and the background noises were reduced. The ability to employ SALDI-MS for analysis of polymer degradation products would reduce sample preparation.

An essential property for a SALDI substrate is conductivity, i.e., the ability to transfer laser energy along the surface to obtain an efficient LDI. Pyrolytic highly

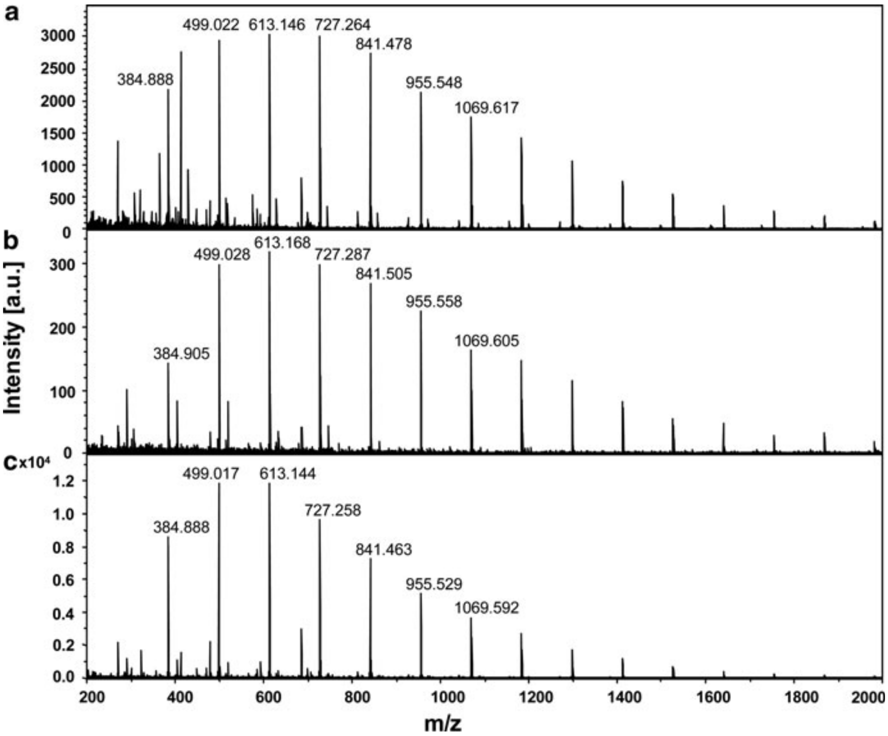

Fig. 6 Mass spectra of polycaprolactone oligomer obtained with magnesium hydroxide as a surface and (**a**) 0.1% TFA (**b**) NaI 1 mg/mL, and (**c**) NaI 10 mg/mL as cationizing agent

oriented graphite polymer film (PGS) is a highly conductive material that has been employed for environmental analysis of low molecular weight compounds by SALDI-MS [29]. In addition, it is a highly oriented graphite film with submicrometer surface roughness. The advantage of PGS is the simple sample preparation, as mentioned earlier for the nanocomposites. Modification of PGS could yield different surface properties and thereby be able to target the analytes of interest. In this study, the surface of PGS was oxidized and modified with the cationic polymer polyethyleneimine in order to improve the sensitivity for detection of environmental compounds. Environmental analysis of perfluorinated acids such as perfluorooctanesulfonic acid, perfluorooctanoic acid, pentachlorophenol, bisphenol A, benzo[α]pyrene, and 4-hydroxy-2-chlorobiphenyl was possible by using PGS SALDI-MS. The PGS SALDI performance was also tested for different carbon chain lengths of perfluoroalkylcarboxylic acid, from C5 to C14. A difference in chain length will also change the hydrophobic properties and may influence the LDI process. The signal intensities decreased as the carbon chain length increased. This could be to do with the hydrophobic chains, because intermolecular forces might be stronger between the surface and the analyte or between the carbon chains and thereby inhibit desorption. For good results, chain lengths below C6 were believed to be suitable for PGS SALDI-MS. Quantitative analysis showed that PGS SALDI-MS allowed the detection of several tens of parts per billion (ppb).

2.2.2 Polymeric Materials

Using polymers and oligomers as surfaces for LDI-MS could be referred to as polymer-assisted laser desorption ionization–mass spectrometry (PALDI-MS) or, as earlier, SALDI-MS [30–33]. Small oligomers have been used for LDI-MS analysis, similar to the matrix in MALDI, of small molecules and no fragmentation or suppression of the mass spectrum was observed (<350 Da). An advantage of this surface technique using polymeric materials is the possibility to characterize nonpolar compounds, since the mechanism involves a charge transfer instead of protonation or metal ion adducts like other surface LDI techniques in positive ion mode. Alkyl-substituted thiophene polymers have been used for analysis of small aromatic complexes, with a sensitivity of 10 nmol. Copolymers and polymer blends of porous monolith structures have been used for matrix-free methods. These are rigid polymers with both micropores and mesopores. Poly(butyl methacrylate-*co*-ethylene dimethacrylate), poly(styrene-*co*-divinyl benzene), and poly(benzyl methacrylate-*co*-ethylene dimethacrylate) monoliths were compared and the latter showed the best potential for LDI analysis. The desorption and ionization of the monolithic polymers depends on the laser power, solvent for the sample preparation, and the pore size of the monoliths. The polymers were effective in laser powers used for typical MALDI analysis. An optimal pore size was approximately 200 nm. In addition, the polymer samples could be stored for a month in ambient conditions without change in the analyte signals. Carbon nanotubes (CNTs) have recently been immobilized in a polyurethane adhesive in order to improve the sample deposition step. The immobilized form of CNTs showed equal SALDI performance as the pure CNTs [34]. Naifion is another carbon-based material incorporated into a polymer matrix [35]. Microparticles of carbon graphite are added to the Naifion polymer. The role of the particles is to absorb the energy and transfer it to the analytes while the polymer donates protons to promote ionization of the analytes.

2.3 Solvent-Free Matrix-Assisted Laser Desorption Ionization–Mass Spectrometry

Solvent-free MALDI methods provide advantages for analyzing polymers that are insoluble such as polyfluorene [36] and large aromatic hydrocarbons [37]. The sample preparation step is simplified and problems that are caused by the solvent are reduced. Compared to the solvent-based methods, a more homogeneous analyte/matrix mixture and higher shot-to-shot and sample-to-sample reproducibility can be obtained with the solvent-free methods [38, 39]. However, this method is still less efficient for samples for which the solvent is not an issue. Also, a lower laser power is applied, which results in milder conditions with less fragmentation compared to the conventional solvent-based methods. The background signals are reduced and the resolution of the analyte signals is improved. The analyte, matrix, and salt are usually mixed by grinding [39, 40] (mortar and pestle), ball-mill, or vortexing [41]. In addition, an enhanced method for sample preparation is the multisample method that is derived from the vortex method. This is a method that facilitates sample preparation and has been used for the evaluation of numerous polymers such as PEG, PS, and PMMA with different molecular weights, and also of polymer additives [42, 43]. However, the transfer of the sample mixture to the MALDI plate is generally made in one of two ways: by pressing a pellet that is affixed to the plate with an adhesive tape, or by transferring the sample with a small spatula and pressing it on the plate to a thin film. The solvent-free MALDI method opens up investigation of new matrices without dependence on the compatibility with the solvent system. In a recent work, analysis of PLA with this method gave very good results and it was possible to follow up the interactions between the matrix and analyte by solid state nuclear magnetic resonance spectroscopy [44].

3 Ambient Desorption Ionization–Mass Spectrometry

One of the most challenging parts of traditional atmospheric pressure ionization sources for analysis of polymer or polymer additives is the requirement of sometimes extensive sample preparation steps prior to analysis. This is the case for ESI, MALDI, atmospheric pressure chemical ionization (APCI) and atmospheric pressure photoionization (APPI). During the last few years, a new generation of ionization methods known as ‘ambient MS’ and ‘direct ionization MS’ have been developed and are summarized in many reviews [45–47]. The specialty of these new ambient techniques is that they do not require any sample preparation so that samples can be directly analyzed in their native, untreated forms. Ambient desorption ionization mass spectrometry operates in open air and is well suited for surface analysis and in situ studies of any size and shape. There exist nearly 30 different ambient techniques today and they are divided into ESI-related techniques and APCI-related techniques. However, the two most emerging tools in ambient ionization mass spectrometry are DESI and DART. These two similar techniques offer qualitative and semi-quantitative analysis, the main difference being the sample preparation. In DESI, liquid samples have to be deposited on a suitable surface, after which they are allowed to dry. Gas samples on the other hand have to be adsorbed into materials. However, no sample preparation is required for solid samples. In DART, no sample preparation is necessary at all.

3.1 Desorption Electrospray Ionization–Mass Spectrometry

DESI was developed in 2004 by Cooks [48] and, as mentioned earlier, is analogous to electrospray ionization, i.e., it is an ESI-related technique. It is a simple and straightforward technique and well-suited for solid samples. It already has a wide applicability, from small molecules to proteomics, and has especially been applied for analysis of polymer surfaces and their surface-active additives. The detection limit for this technique is very low and can be in the order of attomoles [49]. DESI has been combined with different mass analyzers, including quadropoles, triple quadropoles [50], quadropole time-of-flight [51], and a hybrid quadropole linear ion trap [52]. Additionally, DESI has been combined with FTICR [53] and an Orbitrap instrument [54]. In DESI, a solid-phase sample surface is bombarded with a spray of charged microdroplets from an electrospray needle in an ambient environment. The surface is first pre-wetted by initial droplets that will impact the surface; analytes are desorbed and collected from the surface into the droplets. Subsequent droplets will hit these first droplets and break them up and transfer the new droplets containing the analyte molecules to the mass spectrometer inlet for detection. The mass spectrum observed is similar to that in ESI, with both multiple and single charged molecular ions.

3.1.1 Analysis of Polymer Additives

Polymeric materials contain wide range of different additives, some of them added to protect the polymer from degradation or decomposition. Recently, a qualitative and semiquantitative analysis of four common polymer additives (Chimassorb 81, Tinuvin 328, Tinuvin 326, and Tinuvin 770) in concentrations between 0.02% and

0.2% in PP samples was performed with DESI-TOF-MS [55]. DESI parameters such as heating of the polymer and different spray solutions were tested and optimized before analysis. The polymers were heated using a heat gun before analysis to 400 °C for 2–5 s. It was shown that longer heating times increased the signal intensities; however, 5 s of heating could lead to deformation of the sample and thereby decrease the reproducibility. The decomposition and voltage of the DESI solvent spray is another important parameter. The selection depends on the ability to act as a good solvent for the specific analytes in question and on the robustness of spray performance. In this study and for these special analytes, the spray voltage was set to 3,400 V and the solvent was a mixture of methanol, water, and formic acid (80:20:0.1 vol/vol). The investigated polymer samples were used as a liner for an in-ground swimming pool. Calibration curves were constructed for different concentrations for the quantitative analysis. Quantitative analysis of Chimassorb 81 in a liner for an in-ground swimming pool showed a concentration of 0.082%. The result was in accordance with a high performance liquid chromatography–ultraviolet (HPLC-UV) method that was employed in an earlier study and showed a concentration of 0.080% of Chimassorb 81. In addition, quantitative analysis of PP granules was tested, and Tinuvin 770 was found at a concentration of 0.150%. However, HPLC-UV could not be used for verification since it does not work for Tinuvin 770. Instead, another technique, TDS-GC-MS, was tested and the concentration was determined to be 0.148%, verifying the earlier results.

3.1.2 Polymer Samples and Surfaces for DESI

In 2006, the first industrial polymers, such as PEG, poly(tetramethylene glycol) (PTMG) and polyacrylamide (PAM) were analyzed using DESI in solid phase [56]. A paper surface was employed for the analysis of polymer materials. The mass spectrum of PEG showed multiple charged molecular ions with Gaussian distribution. The average molecular weight was calculated to be 3,146, which is in good agreement with the expected value of 3,000. The study of hydrophobic polymers such as PTMG by ESI [57] is very challenging, and since DESI is an ESI-related technique the same results were expected here. Dissolution systems are usually required for the spray solvent in order to avoid discrimination between oligomers with different molecular weights. Also, a low polarity solvent decreases multiple charged molecular ions and thereby limits the mass range. The results reflect these drawbacks; the calculated average molecular weight was 1,412 and the value reported by the manufacturer was 2,900. For the hydrophilic polymer PAM, the same drawback resulted in a measured average molecular weight of 500 that should have been 1,500. The challenges in DESI analysis of higher molecular weight polymers are the discrimination of molecules, the reduction of multiple charged analytes in low polarity solvents, and overlapping peaks.

Structural information on the low molecular weight synthetic polymers PEG, PPG, PMMA, poly(α-methyl styrene) (PMS), and poly(dimethyl siloxane) (PDMS) was obtained with DESI combined with tandem mass spectrometry (MS/MS) [58]. This combination works well and is comparable with ESI, MALDI, and MS/MS ionization techniques. The advantage with DESI over earlier systems is the short time and reduced sample preparation required for studies. Additionally, pharmaceutical tablets made of PDMS can be directly introduced into the DESI source and analyzed in tablet form.

3.1.3 DESI Surfaces

For studies of liquids by DESI-MS, a surface is employed where the analytes are deposit. The quality of the surface in terms of potential, chemical composition, and temperature limits can affect the ionization mechanism. Since charged particles are in contact with the surface, neutralization must be avoided. Neutralization occurs for conductive materials such as graphite and metal materials. However, if the materials are isolated or a voltage is applied on the surface that is equal or lower than the spray voltage, then these materials can be used as substrates. The signal stability is also affected by the electrostatic properties of the surface, whether the surface prefers the polarity of the spray solvent or not.

Polymers have been applied as surfaces, e.g., polytetraflouroethylene [59] is an electronegative polymer that gives high signal stability in negative-ion mode whereas PMMA performs better in positive-ion mode. Additionally, the chemical composition of a surface can affect the crystallization of the analytes when deposited from a solution, resulting in an uneven distribution. The analyte molecules should not have high affinity towards the surface since sensitivity could be lost. Surface roughness is another important parameter that could affect the ionization efficiency. Cooks and coworkers tried microscope glass slides as surfaces before and after HF etching and the results showed that etching increased the signal stability and reduced sweet spot effects. Therefore, a rough surface such as paper is one of the best substrates for DESI. A surface that can work at higher temperatures is preferred because it can increase the ion yield and increase the signal stability; however, this could be analyte-dependent and therefore an optimal temperature should be chosen for the specific study.

3.2 Direct Analysis in Real Time Mass Spectrometry

In 2005, DART was developed as an atmospheric pressure ion source that is suitable for direct analysis of solids, liquids, and gasses in open air conditions [60]. This became one of the first ambient ionization techniques that allow a new source of detection of compounds without the need for sample preparation. The technique is very similar to APCI and APPI but DART-MS offers direct input of samples as mentioned earlier. A unique application of DART has been for direct analysis of chemicals on surfaces without any sample preparation, such as the solvent extraction that is necessary for GC-MS or HPLC before analysis. Among many interesting and successful studies, DART has been employed especially for analysis of additives, stabilizers, and polymer degradation products.

The analysis of samples is based on a reaction between a gas stream, usually helium or nitrogen, and sample molecules at atmospheric pressure. The reaction is initiated in a discharge chamber containing a cathode and an anode where the gas will be exposed to electrical potential and produce electronic or vibronic excited-state species (metastable molecules or atoms). These species can directly interact, desorb, and ionize the sample molecules on the surface. The mass spectrum obtained is usually dominated by protonated molecules in positive-ion mode or deprotonated molecules in negative-ion mode. The advantages of DART are that samples can be desorbed and ionized directly from surfaces and provide real-time information, and that no radioactive components are involved.

3.2.1 Identification of Polymer Additives

Additives are divided into low and high molecular weight compounds with different physiochemical and chemical properties. Therefore, different analytical methods need to be applied. The volatile compounds are usually detected with gas chromatography combined with mass spectrometry (GC-MS) and the nonvolatile compounds with liquid chromatography combined with mass spectrometry (LC-MS). Polymeric food packaging materials contain many different additives such as UV stabilizers, plasticizers, antioxidants, colorants, and grease-proofers that are desirable for the packaging characteristics. Migration of these additives but also monomers and degradation products from the polymeric packaging material to the foodstuff is possible. Therefore, a simple quality control method for screening the presence of undesirable compounds in contact with food would be useful. Different extraction methods in combination with gas chromatography have been used for analysis of migrants; however, some of these can be problematic and time-consuming because the analytes need to be separated from the polymer matrix before analysis. Extraction of chemicals can be selective and competitive displacement could easily occur between the analytes of interest. Another feature is that extraction methods such as headspace GC-MS do not provide surface analysis. An ideal tool for identification of surface contamination by additives is DART-MS. This technique allows direct introduction of solid samples and provides a fast and simple detection of polymer additives.

DART-MS has been successfully applied for the screening of common additives such as Tinuvin 234, di-2-ethylhexyl phthalate (DEHP), di-2-ethylhexyl adipate, Irganox (1076, 1010), Irgafos 168, and Chimassorb 81 from commercially available packaging materials such as PP, low density polyethylene, high density polyethylene (HDPE), PET, polyvinyl chloride (PVC), and polyvinylidene chloride (PVDC) [61]. The spectra of packaging additives produced predominately protonated molecular ions and matched the spectra from standard additives very well. Product ion spectra, DART-MS/MS, were also obtained for the different additives and these matched the standard additive spectra even better. Figure 7 compares the mass

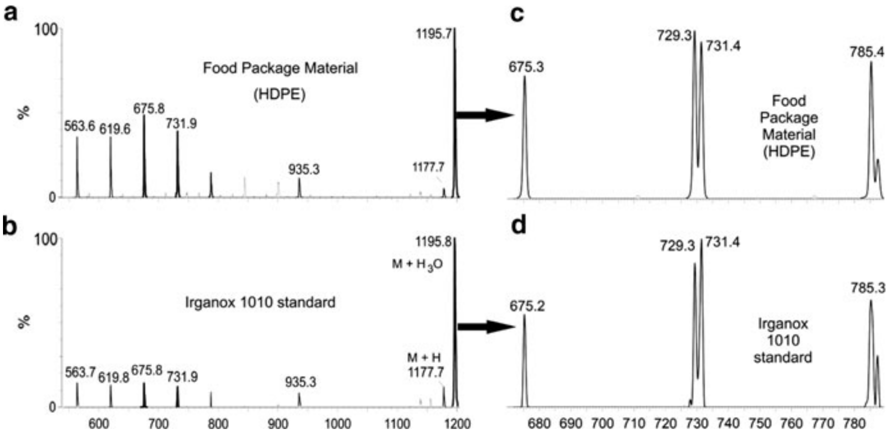

Fig. 7 DART-MS spectra of (**a**) food-packaging material (HDPE) (**b**) Irganox 1010 standard, and (**c, d**) corresponding MS/MS product ion spectra. Reprinted from [61] with permission of Springer. Copyright Springer (2009)

spectrum of the food packaging material of HDPE and the spectrum of the Irganox 1010 standard, and also compares the respective product ion spectra. In another similar study, 21 different stabilizers used for PP were detected with DART-MS. The additives were analyzed both from liquid samples mixed with toluene, and solid polymer samples [62]. The stabilizers analyzed were different Irganox (1010, 1330, 3114, 1035, 1076, 1081, MD 1024, E201, PS 800, and PS 802), Irgafos (126, 38, 168, HP 136, PEP 36, and Chimassorb 81), and Tinuvin (234, 326, 327, 328, and 770) compounds. The study showed that some stabilizers tend to decompose when exposed to high temperatures, high pressures, or oxidizing atmosphere. This led to a reduction of signal intensities, as seen in Fig. 8, and the intensity of some common stabilizers decreased with increasing temperature. This result confirmed that applying high temperatures during polymer processing could lead to a lower additive concentration in the final product. DART-MS also allowed the identification of degradation products from some additives. For example, a spectrum of the polymer sample containing Irgafos 126 and its degradation products such as 2,4-di-*tert* butylphenol were detectable.

Phthalic acid esters (PAE) are common plasticizers used for materials made of PVC. Toys and childcare articles could be made of PVC and there is concern about the migration of these PAE and their effect on human health. There exist different types of PAE and the challenge is to distinguish between the different phthalates. It is essential to be able to distinguish a sample mixture of DEHP, dibutyl phthalate (DBP), and benzyl butyl phthalate from diisononyl phthalate (DINP), diisodecyl phthalate (DIDP), and di-*n*-octyl phthalate (DNOP) because European legislation treats these compounds differently. Recently, toy materials made of PVC were analyzed with DART-MS in order to develop a rapid method for screening of PAE [63]. Figure 9 shows typical DART-MS spectra for DINP, DIDP, and DBP. Toy

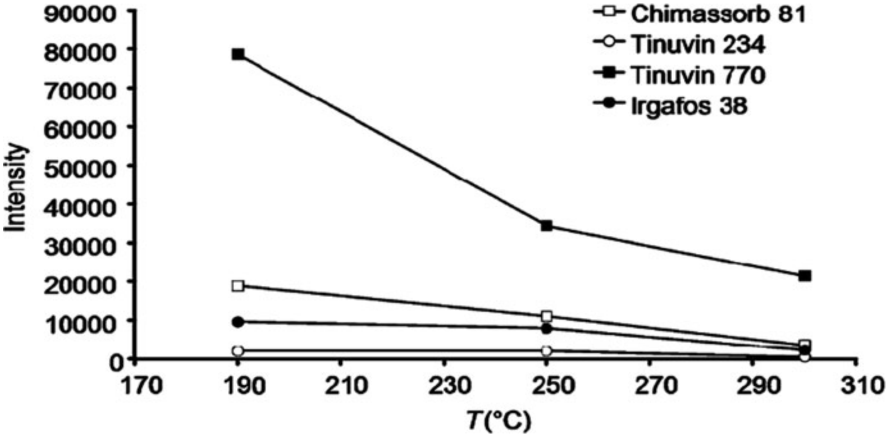

Fig. 8 Degradation of antioxidants due to high temperatures during polymer processing is shown by the reduced signal intensities for some common stabilizers. Reprinted from [62] with permission of The Royal Society of Chemistry. Copyright The Royal Society of Chemistry (2010)

samples were manually introduced in the DART source and the LODs for the protonated phthalate molecules were $\leq 0.1\%$. It was also possible to differentiate between the isomers DEHP and DNOP by their different fragmentation pathways. The same authors have studied lid gaskets of glass jars made of PVC containing diverse plasticizers and other additives, also called plastisols [64]. An interesting finding was the ability to study complex mixtures of polyadipates (PADs) from food packaging materials. PADs are very complex polyester additives and, usually, their identification in foodstuff needs a lot of pre-preparation before mass spectrometry. However, a successful DART-MS analysis was possible.

Chewing gums are delivery systems typically made of polybutadiene or polyvinyl acetate containing several flavor compounds. The volatile flavor compounds are usually studied with GC-MS and the nonvolatile analytes by LC-MS after a sample extraction step. Recently, DART-MS has been applied for the kinetic release study of an apolar cooling agent cyclohexanecarboxamide, *N*-ethyl-5-methyl-2-(1-methylethyl) (WS-3) from chewing gum in saliva [65]. Quantitative analysis of WS-3 in saliva by DART-MS and LC-MS was compared and a good agreement was achieved between the two methods. The DART-MS method could, therefore, become a fundamental technique for investigating delivery systems.

Moreover, DART-MS could be applied for the analysis of insoluble samples that are difficult to analyze with liquid-based methods such as ESI, APCI, and APPI. These techniques require samples to be dissolved in a solvent. During the last few years, solvent-free methods such as solvent-free MALDI have been applied for the analysis of insoluble compounds. However, they are time-consuming and there is a high risk of contaminating the ion source. In a recent study, DART-MS was capable of analyzing insoluble polycyclic aromatic hydrocarbons [66]. It should also be possible to apply this method for analysis of insoluble polymer samples used for food packaging or environmental materials.

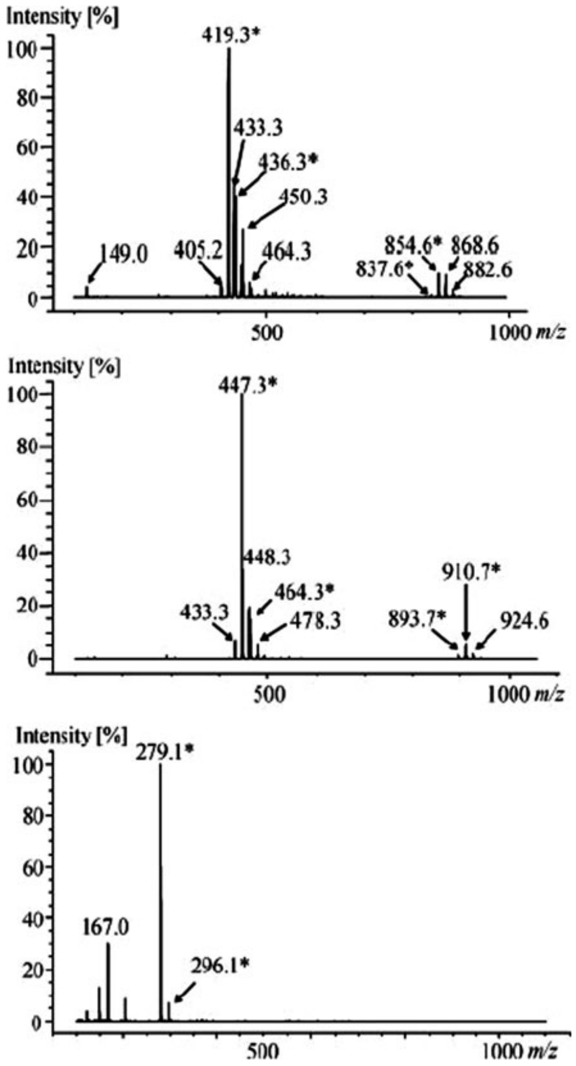

Fig. 9 DART-MS spectra for PAE in toluene: (**a**) DINP, (**b**) DIDP, and (**c**) DBP. The adducts (proton and ammonium) are marked with an *asterisk*. Reprinted from [63] with permission of Springer. Copyright Springer (2009)

4 Fourier Transform Mass Spectrometry and FTICR-MS

In mass spectrometry, the quality and performance of a mass analyzer is very important for analysis of high molecular weight compounds such as polymers. TOF mass analyzers have been used for analysis of synthetic polymers because of their high sensitivity and the wide mass range that can be obtained. However, for analysis of complex polymer samples a mass analyzer such as those used for FTICR-MS or FTMS, with higher resolving power and high mass accuracy, is an advantage. This technique combined with tandem mass spectrometry techniques could offer oligomer determination [67], molecular weight distribution [68], and endgroup analysis [69]. FTMS is usually combined with two tandem mass spectrometry techniques: collision-induced dissociation (CID) and electron-capture dissociation (ECD) [70]. The two fragmentation techniques, CID and ECD, are usually used in combination since they give complementary information. In CID, a selected ion is excited to a higher cyclotron radius (higher kinetic energy) and allowed to collide with a neutral gas (helium, nitrogen or argon). Collisions will lead to a transfer of kinetic energy from the ions to the neutral gas and conversion to internal energy, which will result in bond breakage and fragmentation. There are different ways to increase the kinetic energy of ions but the most common method used in combination with FTICR-MS is sustained off-resonance ion excitation. The ions accelerate in a cyclotron motion and the increased pressure results in CID fragmentation. In coating characterization, complex polymer compositions like copolymers are dominant and mass spectrometry is a routine tool for obtaining information about polydispersity, molecular weight distribution of polymers, and also structural and elemental composition such as repeating units and endgroups. However, for these complex structures a high resolution FTMS combined with tandem mass spectrometry is fundamental [69]. Polyesters are used in automotive coatings and their function is to prevent pigment aggregation and to maintain viscosity.

4.1 Polyphosphoesters in Biomedical Applications

Polyphosphoesters (PPEs) are polymers used in many biological and pharmaceutical applications in drugs, gene delivery, and tissue engineering because of their chemical properties, biocompatibility, and biodegradability. These polymer have structural versatility, and modification in the backbone of PPEs could introduce new bioactive molecules. However, only a small variation in structure can change their interaction with biological systems. PPEs are biodegradable polymers and their performance in biomedical application depends on their properties. They can only be applied if the degradation products are known and nontoxic. Recently and for the first time, FT-ICR mass spectrometry and tandem mass spectrometry (CID and ECD) were applied for the analysis of the polyphosphoester poly[1,4-bis (hydroxyethyl)terephthalate-*alt*-ethyloxyphosphate] [71]. Valuable information on the structure and degradation products was obtained. The polyphosphoester was dissolved in a chloroform/methanol/acetic acid (30:70:2, vol/vol) solution and electrospray ionization was performed. The resulting spectrum was mainly dominated by single charged ions (see Fig. 10). The first spectrum (Fig. 10a) is divided into four different areas 1×P, 2×P, 3×P, and 4×P and these represent the number of phosphate groups for each degradation product. The Fig. 10b shows an expanded version of the 1×P region, with belonging single charged adducts, and Fig. 10c shows the first part of the 2×P region. For CID and ECD fragmentation analysis, cationization was promoted with sodium iodide (NaI) added to the final

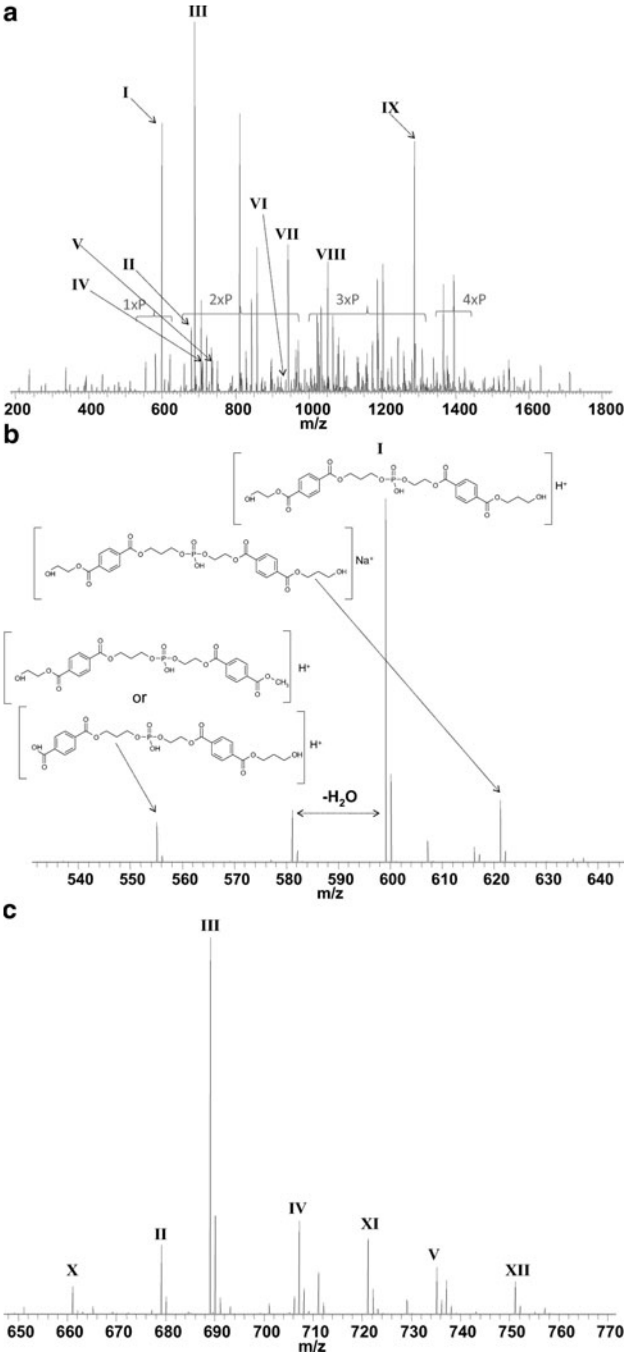

Fig. 10 Electrospray FT-ICR mass spectrum of (**a**) poly[1,4-bis(hydroxyethyl)terephthalate-*alt*-ethyloxyphosphate] in a solution of chloroform/methanol/acetic acid, (**b**) enlarged *m*/*z* region 550–650 and (**c**) enlarged *m*/*z* region 650–770. Reprinted from [71] with permission of Springer. Copyright Springer (2009)

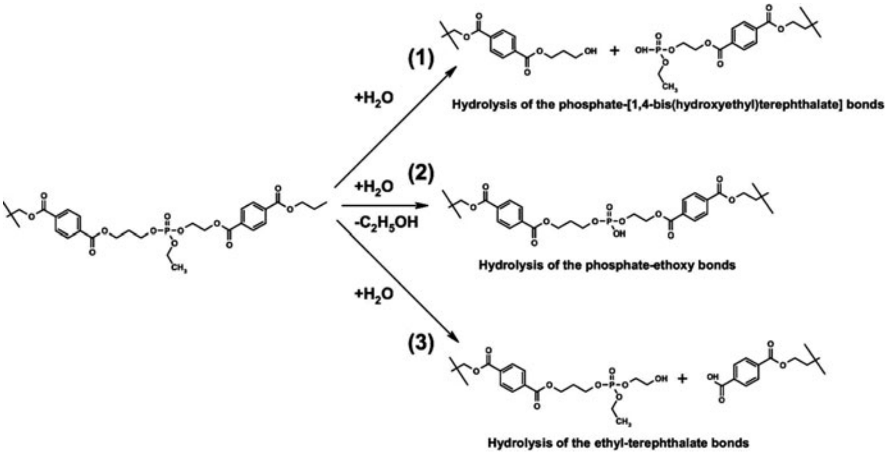

Fig. 11 Degradation scheme of poly[1,4-bis(hydroxyethyl)terephthalate-*alt*-ethyloxyphosphate]. Reprinted from [71] with permission of Springer. Copyright Springer (2009)

electrospray solution: polyphosphoester in chloroform, NaI in water, NaI in methanol, and NaI in acetic acid (30:10:70:2, vol/vol). The molar ratio between polyphosphoester and NaI was approximately 1:1. Additionally, the two fragmentation methods gave detailed information about the structure and the degradation products; see Fig. 11 for the degradation pathway of polyphosphoester poly[1,4-bis (hydroxyethyl)terephthalate-*alt*-ethyloxyphosphate]. The degradation occurred through hydrolysis at phosphate–[1,4-bis(hydroxyethyl)terephthalate] bonds, phosphate–ethoxy bonds, and ethyl–terephthalate bonds. In CID, both single protonated and sodiated PPE ions were observed due to cleavage of backbone C–C bonds. This could also be observed in ECD; however, a larger number of other fragments could be observed, such as cleavage of CH_2–O bonds closest to the terephthalate.

4.2 FTMS Versus TOF

The mass analyzer used plays an important role in the detection of a polymer spectrum. In a recent study, the spectrum of nonpolar polymers with narrow molecular weight distribution such as polyethylene 2,000 (the number is the average molecular weight), polybutadiene 8,300, polyisoprene 8,000 and polystyrene 10,000 were compared [72]. The spectra from a MALDI instrument coupled to either a FTMS or a reflectron TOF mass spectrometer were compared. Low mass fragment ions were found in the spectrum for polyethylene using TOF whereas no fragmentation occurred in the same FTMS spectrum. It was believed that the results were related to the time frame of each mass analyzer, ca. 100 μs/spectrum for TOF and 100–1,000 s of ms per spectrum for FTMS measurements. The fragment ions might

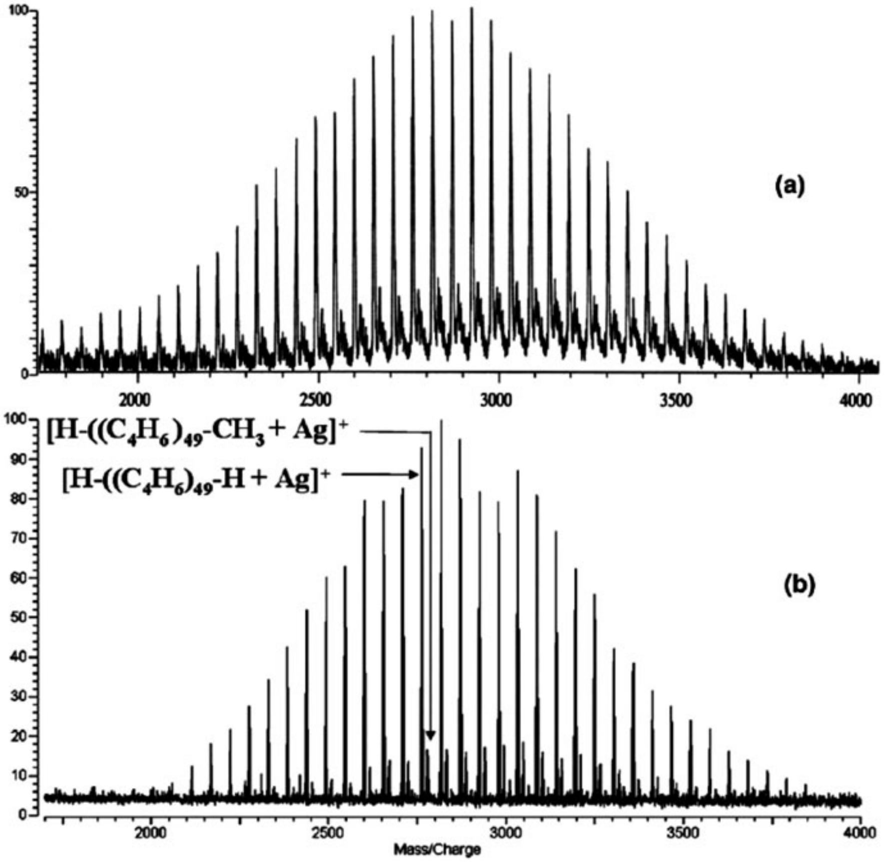

Fig. 12 (**a**) MALDI-TOF spectrum and (**b**) MALDI-FTMS spectrum of polybutadiene (M_n ~2,800) with two distributions of the oligomers having different endgroups. Reprinted from [72] with permission of Springer. Copyright Springer (2005)

not be observed in FTMS because they are often short-lived ions and therefore only seen by the faster TOF. This trend can be observed in Fig. 12 for polybutadiene with average molecular weight of 2,800 in a MALDI-TOF spectrum and a MALDI-FTMS spectrum. Moreover, the other spectra for nonpolar polymers showed better results using MALDI-FTMS with regard to mass accuracy and resolving power compared to MALDI-TOF.

4.3 Analysis of Polymers

A polymer consists of molecules with different molecular weights, and the properties of a polymer can be affected by the width of the molecular weight distribution and also by the composition of endgroups. Characterization of synthetic polymers has been performed by MALDI FTICR-MS [73]. However, the feature with this combination is the single charged peaks and therefore it is limited to polymeric systems with lower molecular weight. Another ionization technique that would overcome this problem is the combination of ESI with FTICR-MS. In ESI, multiple charged ions are formed, enabling detection at lower mass-to-charge values, which is advantage. This combination also provides a higher accuracy and a high resolution in order to distinguish between the isotopic peaks of the oligomers in different charged states. Molecular weights up to 23,000 could be observed with a setup of ESI with FTICR-MS [74]. Monomer and endgroup characterization of PEG, PPG, and poly(tetrahydrofuran) were also studied by ESI FTICR-MS [75]. Two methods were developed in order to evaluate the monomer and endgroup compositions: a linear regression method and an averaging method for ESI FTICR-MS. The results showed a threefold increase in accuracy with this new combination of ESI with FTICR-MS compared to earlier MALDI FTICR-MS. ESI-FTICR-MS has also been applied for fragmentation observations of homopolyester oligomers, poly (dipropoxylated bisphenol A/isophthalic acid) and poly(dipropoxylated bisphenol A/acipic acid) and the copolyester poly(diproxylated bisphenol A/isophthalic acid/adipic acid) [76].

Oxidation reactions in polymeric materials are important to understand because they could affect the mechanical properties of materials. The concern in these reactions is the release of toxic volatile organic compounds (VOCs). The reaction pathway of thermal oxidation of PP is of high interest, and proton transfer reactions combined with FTICR are a suitable tool for the analysis of complex mixtures of VOCs in air. Recently, thermal degradation of PP samples were studied for real time characterization and quantification of emitted VOCs [77]. The four VOCs found were acetone, formaldehyde, acetaldehyde, and methylacrolein. The advantage of this technique over GC is the detection of very volatile compounds, such as formaldehyde, and of course the rapid real time analysis.

5 Inductively Coupled Plasma–Mass Spectrometry

ICP-MS is a multi-element detection technique that is sensitive and specific. It can detect analytes at very low detection limits, from sub-parts per billion to sub-parts per trillion. This is a practical technique used for analysis of elements, such as heavy metals, in polymers.

5.1 Brominated Flame Retardants

BFRs have been widely used as additives in commercial materials to prevent fire in building materials, textiles, paintings, and electrical components [78]. These compounds could be aromatic, aliphatic, or cycloaliphatic with different bromine content. BFRs could seriously impact our environment and human health. Therefore, a rapid method for analyzing traces of bromine is essential. BFRs such as polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs) are examples of BFRs used to prevent fire in different materials. The Restriction of Hazardous Substances Directive (2002/95/EC) has limited the concentration of maximum BFRs to 0.1 wt% of homogenous material.

A flow-injection ICP-MS has recently been applied for the screening of polyurethanes containing different concentrations of bromine [79]. An advantage of ICP-MS is that there is no need for a matrix calibration, whereas many other techniques require a matrix-matched standard. Here, a low-cost bromide salt is used for calibration. The analytical performance demonstrated that the detection limit for bromine was 4 mg kg^{-1}. Flow-injected ICP-MS is a fundamental technique for screening of bromine-positive samples. Techniques such as GC-MS could provide more information and the exact identity of the additives or additive degradation products [80]; however, ICP-MS is a faster option just for detection proposes as the sample preparation needed in GC-MS is avoided.

The major separation techniques used for analysis of BFRs are GC and HPLC coupled to different detectors (MS, ECD, DAD/UV) [81–88]. However, using ICP-MS as a detection tool is a great advantage since this technique offers a compound-independent response. This method does not experience any interference from other co-eluted halogenated compounds (non-bromine). Therefore, it is not necessary to resolve the chromatogram of the BFRs from other interfering halogenated compounds. Both GC-ICP-MS and HPLC-ICP-MS have been applied for the analysis of BFRs. However, thermal degradation of brominated compounds is a concern when using GC-MS and GC-ECD. PBDEs have been successfully determined with GC-ICP-MS [89] but thermal degradation of highly brominated compounds is still a concern. HPLC-ICP-MS could be a promising method since it overcomes these degradation problems and the injection is done at room temperature. This accurate method for detection of BFRs in polymers has recently been demonstrated [90]. An ultrasonic-assisted extraction (UAE) was employed before introduction to HPLC-ICP-MS for detection of PBDEs and PBB additives in HDPE, PS, acrylonitrile-butadiene-styrene copolymer (ABS), and PP. Solutions of different PBDEs were analyzed: PBDE-47, PBDE-99, PBDE-100, PBDE-153, PBDE-154, PBDE-183, PBDE-196, PBDE-197, PBDE-203, PBDE-206, and PBDE-207 and also PBB-209. However, the LOD and the limits of quantification (LOQ) with this method were higher compared to the earlier GC-ICP-MS, GC-ECD, and GC-MS methods but still within the range that is required from the Restriction of Hazardous Substances Directive (2002/95/EC). But, thermal degradation of the highly brominated compound, PBDE-209 in this case, was not observed.

Another concern when analyzing polymeric materials is traces of inorganic compounds, such as heavy metals (Cd, Cr, Hg, and Pb) that can originate from additives, fillers, colorants, stabilizers, plasticizers, anti-oxidizing agents, and catalyst residues due to toxicity of these elements. Wet chemical analysis is the most common method for determination of metal concentration in products. However, digestion may lead to loss of elements and is therefore a time-consuming method. During the last decade, laser ablation–inductive coupled plasma–mass spectrometry (LA-ICP-MS) has been used for bulk analysis of plastic materials. Also, two suitable polyethylene reference materials containing several heavy metals have been developed for calibration (European Reference Material (ERM)-EC680 and ERM-EC681), which could improve the analysis. In a recent study, ERM was utilized for analysis of real samples such as polyethylene bags, ABS, and plastic toy bricks [91]. LA-ICP-MS was found to be a suitable technique for tracing metal elements in polymeric materials with a concentration level of sub-micrograms per gram to tens of thousands of micrograms per gram. Besides the ERM, internal standards may also be required if the composition of the sample of interest differs from polyethylene. Waste polymer materials, glass, and polyethylene-based materials have also been studied with LA-ICP-MS using external standards [92].

6 Secondary Ion Mass Spectrometry

Secondary ion mass spectrometry (SIMS) is a surface-sensitive analysis technique for composition analysis of the uppermost atomic layer of thin films. The conventional SIMS can operate in two different modes: static mode or dynamic mode. The static SIMS mode provides information about molecular composition whereas the dynamic mode gives elemental and isotopic information. A target plate containing a polymer is bombarded by a primary ion beam (argon or cesium ions) and secondary ions are produced from the surface. The secondary ions are positive ions, negative ions, electrons, and neutral species. TOF-SIMS is a promising method for polymer surface analysis and has been widely used for characterization of molecular weight and endgroups of ethylene–propylene polymers [93], surface crystallization of poly (ethylene terephthalate) [94], specific interactions at the polymer surface [95], modifications of polymer surface [96], contaminants [97], polymer additives [98], detailed structural analysis [99], and surface quantitative analysis of degradation products [100]. Interesting research has been carried out to understand physiochemical surface interactions between degradable biopolymers and biological environments. Hydrolytic degradation of poly(α-hydroxy acid)s such as poly (glycolic acid) (PGA), poly(L-lactide acid) (PLLA) and poly(lactide-*co*-glycolic acid) (PLGA) in different pH buffers were analyzed with TOF-SIMS. It was possible to distinguish and identify the degradation products by their characteristic ion fragmentation patterns. In addition, the interpretation of static SIMS mass spectra can be challenging due to many peaks from fragmented species and therefore depends on making comparisons with spectra from library databases. The chance to find a similar spectrum is low because of library limitations. Recently, an emerging tool known as gentle-SIMS (G-SIMS) has been employed for easier interpretation of static SIMS spectra. The mass spectrum of static SIMS contains mass peaks from degraded and rearranged fragments with high intensities, thus, the identification of the surface becomes difficult. Using G-SIMS, most of these mass peaks can be removed and a cleaner spectrum obtained. Details of G-SIMS can be found elsewhere and its capability has been described for different materials including polymers and Irganox 1010 [101–103]. In a recent study, static SIMS and G-SIMS have been compared for studies of related biodegradable homopolyesters including PGA, PLA, poly-β-(hydroxybutyrate) (PHB), and PCL [104]. However, in spite of the difficulties of the static SIMS it has been the method of choice for surface analysis of polymers. Recently, qualitative and quantitative surface analysis of individual PCL nanofibers was performed in detail [105].

Besides a range of studies using static SIMS, the dynamic SIMS has shown great potential to increase the understanding of stabilization of polymeric dispersions. Polymer surfactants can be used to stabilize polymer blends since polymers are often immiscible in one another. A copolymer surfactant or compatibilizer at a polymer–polymer interface of two homopolymers of polybutadiene has been investigated, with focus on the adsorption and desorption dynamics of the copolymer [106]. Another limitation or challenge with SIMS is the yield of secondary ions. During the last two decades, researchers have tried to develop ways of increasing the yield of secondary ions. The different methods to enhance this have been polyatomic projectiles [107], matrix-enhanced SIMS [108], use of noble metal substrates, and metal-assisted SIMS [109].

6.1 Cluster Secondary Ion Mass Spectrometry

Cluster SIMS introduces new molecular sources $\left(C_{60}^{+}, Au_{3}^{+}, Bi_{3}^{+}\right)$ compared to the conventional ion beam in SIMS $\left(Ar^{+}, Cs^{+}, Ga^{+}\right)$. Polymer analysis by cluster beams is a successful method within SIMS that provides in-depth molecular information; the procedure of cluster SIMS is explained elsewhere [110]. The first molecular depth profiling was carried out on PMMA samples. Cluster ions compared to the conventional ion beam could increase the molecular signal for analysis of polymer-based systems. This has recently been demonstrated in a study of drug-loaded cardiac stents based on poly(styrene-*co*-isobutylene) doped with paclitaxel [111]. It was actually impossible to observe any signals with the conventional SIMS. The molecular signals could also be improved in cluster SIMS by applying a thin layer of a metal such as Au or Ag, a technique known as metal-assisted SIMS [112, 113]. Matrix-enhanced SIMS is another way to enhance the signal by placing the sample in a matrix such as sinapic acid, similarly to MALDI [114, 115]. The metal-assisted SIMS has recently been employed on the surface of polymer-based systems including PS, PE, and PP [116–118]. Cluster SIMS has been used for cleaning of contaminants from the surface. Several studies have demonstrated the ability to remove polydimethylsiloxane from contaminated samples including PLA [119] and PLGA [120]. It is also a promising technique for molecular depth profiling of drug delivery systems. In addition, cluster ions could be used to remove damage created by atomic ion beams [121].

7 Ion Mobility Spectrometry–Mass Spectrometry

Complexity of polymer structures has increased in order to tailor desirable properties and functions for ever more demanding applications [122]. However, the complexity also results in more challenging structural analysis. The introduction of mobility separation prior to mass spectrometric analysis facilitates the analysis of more complex polymer systems [123]. IMS-MS has the ability to extend the dynamic range and separate isomeric compositions and therefore has an advantage over many high-resolution mass spectrometers. Ion sources such as ESI could be combined with IMS-MS to detect more complex chemistries such as copolymers. This combination has been employed for analysis of biomolecules and biopolymers [124, 125]. IMS-MS has recently been combined with ESI to examine distributions of PEG with masses of 6,550 and 17,900 Da and to evaluate the existing oligomers within the polymer matrix [126]. PEG has also been analyzed with IMS-MS in other studies [127, 128]. Furthermore, high resolution IMS-MS has been employed for analysis of PMMA [129]. It was possible to obtain detailed endgroup information, and discrimination of molecules with same nominal masses was possible without time-consuming LC separation prior to analysis. A benefit with IMS is the possible combination with a solvent-free sample preparation, as described for solvent-free MALDI (Sect. 2.3), since IMS is a solvent-free gas-phase separation.

8 Future Perspectives

Mass spectrometry has in recent years become an irreplaceable tool for characterization of increasingly advanced polymer structures, polymer additives, and degradation products. However, we are still far from utilizing the full potential of mass spectrometry in the structural analysis of polymers and their multidimensional complexity. The field of mass spectrometry has experienced enormous development in the last years, with several highly interesting mass spectrometric techniques arriving and being applied for polymer analysis. Some of the most interesting techniques with huge potential in polymer analysis include new developments in LDI techniques, like solvent-free MALDI and SALDI-MS. Another highly attractive possibility is to analyze solid samples in their native form by techniques like DESI-MS and DART-MS. Mass spectrometry already has its given place in the analysis of chemical structures, endgroups, copolymer compositions, molecular masses, and polymer compositions including additives and degradation products. In the future it will surely further strengthen its position as a polymer characterization tool.

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