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Analysis of Polymer Additives and Impurities by Liquid Chromatography/Mass Spectrometry and Capillary Electrophoresis/Mass Spectrometry

Wolfgang Buchberger and Martin Stiftinger

Abstract The analysis of polymeric materials can be quite challenging because such samples are often of complex nature due to the presence of various groups of additives, compounding ingredients, and fillers. Of special importance are stabilizers that protect the material from degradation by thermal stress during manufacture or from environmental impact during use. Apart from intact stabilizers, the degradation products of stabilizers should also be identified to understand the reactions occurring in a polymeric material. In all cases, the optimization of performance of a polymer as well as the reduction of production costs requires adequate analytical methods, whereby high-performance liquid chromatography plays a major role. As outlined in this review, mass spectrometry with atmospheric pressure ionization has become state-of-the-art for identification of components in polymeric materials after separation by liquid chromatography. These ionization techniques include electrospray ionization, atmospheric pressure chemical ionization, and atmospheric pressure photoionization. The latter technique shows various advantages such as low detection limits and applicability to a wide range of structurally different polymer additives. Besides chromatography, capillary electrophoresis has demonstrated some potential for separation of polymer stabilizers and for characterization of polymers, but its importance is still limited in comparison with liquid chromatography. As an alternative to the combination of chromatography with mass spectrometric detection, direct mass spectrometric techniques for solid polymer samples are emerging. These techniques provide new tools for quick screening procedures at the same time as avoiding tedious sample preparation.

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Contents

Abbreviations

APCI	Atmospheric pressure chemical ionization
APPI	Atmospheric pressure photoionization
ASAP	Atmospheric solid analysis probe
CE	Capillary electrophoresis
CZE	Capillary zone electrophoresis
DART	Direct analysis in real time
DESI	Desorption electrospray ionization
EOF	Electroosmotic flow
ESI	Electrospray ionization
GC	Gas chromatography
HALS	Hindered amine light stabilizers
HPLC	High-performance liquid chromatography
MALDI	Matrix-assisted laser desorption/ionization
MEEKC	Microemulsion electrokinetic chromatography
MEKC	Micellar electrokinetic chromatography
MS	Mass spectrometry
NP	Normal phase
RP	Reversed phase
SEC	Size-exclusion chromatography

SFC	Supercritical fluid chromatography
SIMS	Secondary ion mass spectrometry
TOF	Time-of-flight
UHPLC	Ultrahigh-performance liquid chromatography

1 Introduction

The importance of polymeric materials for various applications in everyday life has continuously increased over the last decades. These materials provide significant benefits, such as being durable and lightweight with an excellent cost/performance ratio. At a first glance, many technical polymers may seem to be of chemically simple composition, but polymeric materials can be complex samples containing numerous additives that are responsible for the final physical and chemical properties as well as for the long-term behavior. Among these additives are nucleating agents that provide control over the formation of crystals; antistatics that prevent build-up of static electricity by interacting with atmospheric moisture; slip and antiblocking agents for easier manipulation of the polymer; acid scavengers that protect manufacturing devices from corrosion; flame retardants; compounding ingredients including mineral fillers or glass fibers; color pigments; and stabilizers. Stabilizers are of utmost importance because several polymers would be significantly impaired by degradation processes if no stabilizers were added. Typical stabilizers include phenolic antioxidants that scavenge radicals, organophosphites that decompose peroxides, and light stabilizers such as benzophenone derivatives, benzotriazol compounds, and hindered amine light stabilizers (HALS) that protect the material against photooxidation. The structures of a few typically employed stabilizers are given in Fig. 1 together with common trade names (although these compounds may also be available under different trade names).

The analysis of additives (and especially of stabilizers) can be approached at in two different ways. On the one hand, there is an obvious need for target analysis (quantitative determination of known additives) for quality control during the production process of polymers and polymeric materials, as the lifetime of a plastic component may be directly related to the presence of a sufficiently high concentration of a certain stabilizer. On the other hand, non-target analysis (qualitative and quantitative analysis of unknown species) becomes a matter of concern when products of competitors must be characterized or when degradation pathways of additives (stabilizers) are investigated in order to obtain a better understanding of the reaction mechanisms of stabilizers in a polymer. A better knowledge of degradation products helps to avoid an insufficient stabilizer performance and to select the most appropriate ones for a certain application.

Generally, the determination of additives and possibly unknown degradation products in plastic materials is a challenging task in analytical chemistry due to the widely differing chemical structures of additives. From the practical point of view,

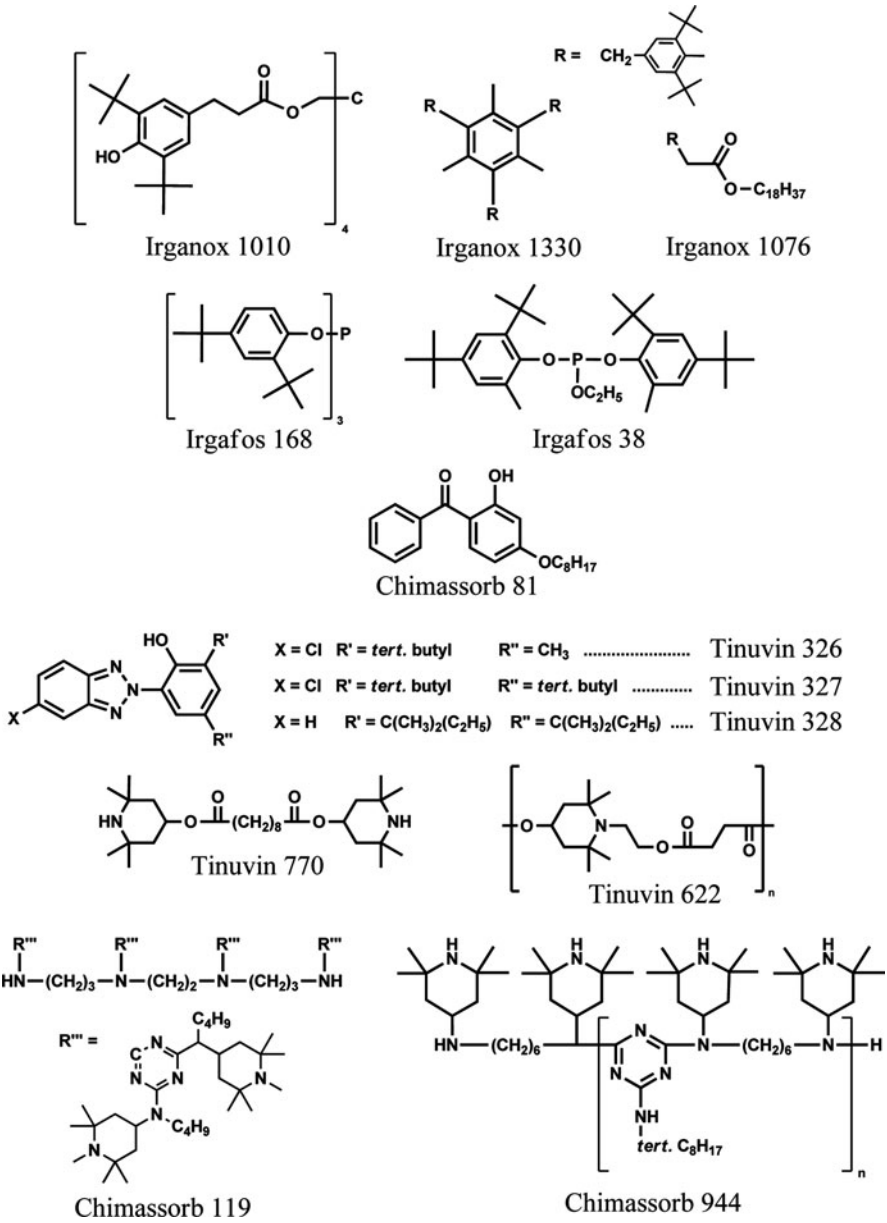

Fig. 1 Structures of various antioxidants (Irganox 1010, Irganox 1330, Irganox 1076), organophosphite process stabilizers (Irgafos 168, Irgafos 38), a benzophenone-type light stabilizer (Chimasorb 81), benzotriazole-type light stabilizers (Tinuvin 326, Tinuvin 327, Tinuvin 328), and hindered amine light stabilizers (Tinuvin 770, Tinuvin 622, Chimasorb 119, Chimasorb 944)

methods that can directly analyze additives in the solid sample without sample preparation would be most attractive. Unfortunately, such methods are not yet widely available or may not be sensitive enough to measure stabilizers typically present at concentration levels of a few tenths of a percent. In many cases, extraction of the analytes from the polymeric material or dissolution of the whole sample may be necessary. Due to the superior chemical stability of various technical polymeric materials, dissolution can become a main obstacle within the analysis. Also, extraction processes without dissolution of the whole sample can be quite tricky, and it may be difficult to prove that the extraction of the analyte is indeed quantitative. Even if sample preparation steps are available to get the analytes into solution, the subsequent determination step, typically based on chromatographic procedures, is far from trivial. Most additives are only slightly volatile and therefore not suitable for gas chromatographic (GC) analysis. Consequently, separation techniques operating in the liquid phase, including high-performance liquid chromatography (HPLC) and capillary electrophoresis (CE), are preferred. Although HPLC methods have become a routine tool for determination of additives in technical polymers, there is still no single stationary phase or single detection mode that allows simultaneous separation of the whole range of chemically different additives typically used for polymers.

This review deals with novel HPLC and CE methods for analysis and determination of additives in polymers. The possibilities of their use in conjunction with mass spectrometry (MS) are presented, with emphasis on achieving confirmation of additive identity, improving detection limits in the case of target analysis, and structure elucidation for unknown chromatographic peaks in the case of non-target analysis. Special attention will be paid to stabilizers, which are the additives most frequently analyzed for routine purposes.

2 Sample Preparation Prior to Chromatographic Analysis

As mentioned in the Introduction, a common approach to sample preparation for chromatographic analysis of additives is the dissolution of the total polymeric matrix, with all the different components present. Subsequently, the polymer can be precipitated by addition of an appropriate solvent that decreases the solubility of the polymer but still acts as a good solvent for the additives so that quite clean solutions for analysis are obtained. Depending on the chemical nature of the polymer, good solvents for dissolution of the whole sample may be difficult to find. Furthermore, polymers sometimes become strongly swollen rather than completely dissolved when treated with an organic solvent.

A typical procedure based on dissolution and precipitation for determination of stabilizers in polyolefins [1] includes the treatment of a 500 mg sample with 50 mL

toluene by refluxing. Subsequently, the solution is cooled and mixed with 25–50 mL of methanol. After filtration, an aliquot of the filtrate is evaporated to dryness and reconstituted in 0.5 mL of appropriate solvent for chromatographic analysis. Various similar procedures can be found in the literature for polyolefins using xylene or toluene for dissolution and methanol for precipitation [2, 3]. Depending on the type of polymer, other more aggressive solvents such as chloroform [4] or hexafluoropropanol/dichloromethane [5] have been suggested for dissolution, followed by precipitation using methanol or acetone. Such sample preparation strategies have been used for many years and are included in a review by Vandenburg et al. [6] prepared almost 15 years ago. More recently, it has been demonstrated that this dissolution/precipitation approach can also be miniaturized and applied to depth-profiling of stabilizers in polymeric materials using microtome slices [7].

In the case of HALS, the polymer can be completely dissolved in an appropriate solvent, followed by a liquid–liquid extraction step with aqueous sulfuric acid, which allows selective extraction of the analytes into the aqueous phase (see for example [8]).

Instead of using the total dissolution/precipitation approach, additives may also be extracted in a more selective way from the polymer by solid–liquid extraction using various techniques. In these cases, it is essential to decrease the particle size of the sample by grinding down to approximately 0.5 mm, preferentially with cooling by liquid nitrogen to avoid thermal degradation of the analytes. Traditional reflux or Soxhlet extraction, ultrasonic extraction, and more recent techniques like accelerated solvent extraction (sometimes called pressurized fluid extraction or enhanced solvent extraction) [9–12] and microwave-assisted extraction [12–14] have been applied for analysis of additives in polymer materials and have found their way into standard methods such as ASTM D7210-06. Supercritical fluid extraction has also demonstrated its potential for extraction of additives from polymers [15–17], although it requires equipment that is more expensive in comparison with other techniques.

3 HPLC/MS of Additives in Polymers

MS detection after liquid chromatographic separation is state-of-the art in modern instrumental analysis. Among the various interfaces and ionization sources developed over the last few decades for combination of HPLC with MS, only ionization sources working at atmospheric pressure, like electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI), and atmospheric pressure photoionization (APPI), are nowadays used in routine analysis. Generally, the compatibility of mobile phases with the various ionization sources must be critically evaluated and optimization of mobile phase composition must be done with respect to both maximum separation selectivity/efficiency as well as maximum MS response.

3.1 HPLC Separation Modes for Additives in Polymers

Reversed-phase (RP)-HPLC using alkyl-modified silica as stationary phase has been the most widely used chromatographic system for the separation of various additives in polymers, particularly stabilizers. This is underlined by the fact that RP-HPLC is recommended in standard methods such as ASTM D6042-09. Typically, acetonitrile/water gradients are used. A comparison of acetonitrile/water and methanol/water gradients [18] indicated that the latter yields somewhat poorer separations, although this is not necessarily the case for every application. The main point in optimizing such separations is the optimization of the gradient conditions (time, steepness), which strongly depend on the type of RP material used (C18-materials from different manufacturers exhibit somewhat different separation selectivities so that gradient conditions must be adjusted accordingly). Some attempts have also been made to optimize the separation by using the column at elevated temperatures or applying thermal gradients [19].

Current trends in RP-HPLC of polymer additives point to the use of ultrahigh-performance liquid chromatography (UHPLC) using stationary phase particles of about 1.7 μm diameter (see for example [20]). Thereby, the efficiency (number of theoretical plates) is significantly increased and shorter columns leading to shorter analysis times can be employed. The disadvantage is the fact that the backpressure generated by UHPLC columns is considerably higher, which necessitates adequate hardware. Furthermore, UHPLC requires the strict elimination of dead volumes in the system. This may be less difficult if a UV detector is used, but ionization sources for MS may contribute to extra-column peak dispersion so that all the benefits of UHPLC columns are not fully available. As an alternative, particles with a nonporous core and a porous shell (core–shell particles, also known under the trade name Fused-Core particles) lead to less backpressure but still are more efficient than traditional particles used in HPLC. The advantages of such core–shell particles for routine analysis of various stabilizers of polymeric materials have recently been investigated [18].

Besides RP-HPLC, normal-phase (NP)-HPLC has also been used for separation of stabilizers (see for example [10, 21]). Although this approach may be advantageous as most stabilizers are easily soluble in typical NP mobile phases, its importance seems to be minor. In addition, NP-HPLC is not fully compatible with some ion sources nowadays used for MS detection.

Supercritical fluid chromatography (SFC) may also have some potential for separation of polymer additives both in the capillary column as well as in the packed column format, as demonstrated several years ago [22, 23]. Nevertheless, this technique has not fully found its way into routine analysis.

3.2 Detection by Electrospray Ionization/Mass Spectrometry

In many cases, polymer additives are nonpolar substances that are less suitable for ESI. An exception is the group of HALS compounds that are readily detected by

ESI in the positive mode due to the presence of protonable nitrogen atoms in the molecule structure. Andersen et al. [24] developed a RP separation of two HALS compounds by capillary RP-HPLC with time-of-flight (TOF) MS detection using a mobile phase consisting of ethylacetate/acetonitrile/triethylamine/acetic acid (45:44.9:10:0.1 v/v/v/v). The use of an amine in the mobile phase to block active sites on silica-based RP stationary phases in order to achieve good peak shapes may lead to ionization suppression in ESI. Therefore, mobile phases without the addition of an amine might be an advantage. Recently, Noguerol-Cal et al. reported the use of HPLC with a mobile phase consisting of water and methanol with 1% formic acid [25] for coupling with an Orbitrap MS. Unfortunately, under such chromatographic conditions the separation performance deteriorates considerably. An alternative to the use of mobile phases containing an amine would be the use of mobile phases at high pH, above the pK_a values of the HALS compounds. Reasonable peak shapes can indeed be achieved under such conditions with a gradient of an aqueous phosphate solution adjusted to pH 11 and acetonitrile [25], but these conditions are hardly compatible with ESI. Reisinger [26] has demonstrated that even a gradient of 0.005 M KOH in methanol and aqueous 0.01 M KOH can achieve a separation of HALS analytes on a stationary phase based on pH-stable methacrylate functionalized with C18 groups. In this case it would be possible to use a suppressor (well-known from suppressed conductivity detection in ion chromatography [27]) between the column and the ESI so that KOH is converted to water prior to entering the ion source. So far, this approach has not yet been investigated in detail but is an attractive approach to be studied in future work.

In the case of Tinuvin 770, which is a relatively simple HALS, Gill et al. [28] developed a RP-HPLC-ESI/MS method using a mobile phase of aqueous ammonium acetate and methanol under gradient conditions, and validated this method for quantitation in migration studies of the stabilizer from a polymeric material into water.

Another area where ESI may be appropriate is the characterization of antistatic additives such as glycerol monostearates, sorbitan fatty acid esters, or ethoxylated alkyl amines. These additives are typically used in polymeric materials as complex mixtures, so that appropriate methods based on HPLC/MS are required for quality control of the additives. Methods have been recently developed for such purposes [29], although applications regarding the quantitation of the additives in polymeric materials are still missing.

HPLC-ESI/MS may also be the method of choice for detection of perfluorooctanoic acid in polytetrafluoroethylene polymers [30]. In this case, perfluorooctanoic acid may occur as an impurity rather than an additive.

Himmelsbach et al. [31] have systematically compared the ESI behavior of various phenolic antioxidants, organophosphites, and benzotriazole light stabilizers with their behavior in APCI and APPI. ESI turned out, as expected, to be inferior to APCI and APPI. On the other hand, the poorer detection limits of ESI do not necessarily exclude its suitability for certain applications such as the analysis of antioxidants in insulation cladding of copper wire [32].

A way around the poor response of nonpolar compounds in the ESI mode is the use of coordination ion spray (CIS). In this case, a common ESI source is used, but after the HPLC column the addition of ions, typically Ag^+, leads to the formation of stable complexes with the analytes and to the ionization. An application to polymer analysis has been reported by Hayen et al. [33] who investigated the behavior of bis-(3-triethoxysilylpropyl) tetrasulfide, a widely used coupling reagent for silica-reinforced rubber materials, and related compounds as well as their reaction products during rubber vulcanization processes.

3.3 Detection by Atmospheric Pressure Chemical Ionization/Mass Spectrometry

In most cases, when MS detection has been employed for determination of additives in polymeric materials, APCI has been used. Its advantages for additives like phenolic antioxidants, organophosphites, benzotriazole compounds, erucamide, oleamide, and oleylpalmitamide have been demonstrated by Block et al. [34] who were able to compile a library of MS spectra of polymer additives. The response of brominated and phosphate-based flame retardants has been studied by Schlummer et al. [35] using RP-HPLC as well as size-exclusion chromatography (SEC) coupled to RP-HPLC. The wide field of applications of APCI in polymer analysis, including even NP chromatography, has recently been outlined by Desmazieres et al. [36], although the focus of that paper was on the polymers and not on the additives. APCI/MS detection has also been successfully applied to separations done by SFC [23].

Duderstadt and Fischer [37] have investigated the impact of the composition of the mobile phase typically employed in RP chromatography on the signal intensities achieved by APCI/MS for selected additives used in polyalkenes. For the positive ionization mode, they tested gradients of water with acetonitrile, methanol, or acetone. In addition, acetonitrile-based mobile phases with post-column addition of methanol were investigated. In the negative ionization mode, the same mobile phases as for positive ionization were employed with the exception of post-column addition of methanol. For the analytes responding in the positive mode, mobile phases based on methanol demonstrated the highest universality, and at the same time yielded the highest response in nearly all cases. In the negative ionization mode, the number of detectable analytes was generally lower, but again methanol-based mobile phases turned out to be best suited. Post-column addition of methanol to mobile phases based on acetonitrile did not lead to results as good as those for mobile phases based on methanol. It should be noted that these investigations primarily focused on a maximum in signal intensities. Highest signal intensity does not necessarily lead to lowest detection limits because the noise of APCI detection must be taken into account and signal/noise ratios do not necessarily depend in the same way on mobile phase composition as signal intensities.

A detailed study of detection limits for polymer additives using APCI/MS detection has been carried out by Himmelsbach et al. [31] and data have been compared with APPI/MS (see discussion in the next section).

3.4 Detection by Atmospheric Pressure Photoionization/Mass Spectrometry

APPI is the latest technology introduced for atmospheric pressure ionization MS [38] and has expanded the range of analytes accessible to HPLC/MS considerably. In many cases, both polar and nonpolar analytes can be analyzed with satisfactory efficiency so that this ionization source has become increasingly popular over the last few years in various application areas [39, 40].

APPI is achieved by photons emitted from a krypton lamp that can interact with the vaporized mobile phase of the HPLC and with the analytes. In the positive ionization mode, direct ionization of the analyte is possible by the photons. Alternatively, a dopand can be added to the mobile phase that is preferentially ionized and, in a second step, ionizes the analyte via charge transfer or proton transfer. Furthermore, the ionized dopand can react with solvent molecules of the mobile phase, thereby forming protonated solvent clusters that ionize the analyte via proton transfer. In the negative ionization mode, direct ionization of the analyte by electron capture is possible. Alternatively, the electrons generated during dopant photoionization may interact with oxygen and yield superoxide ions that can ionize the analyte via deprotonation or by electron transfer. Superoxide ions may also react with analytes in a way that H, Cl, Br, or NO_2 is split off and oxygen is attached. Details of the ionization mechanisms can be found in the recent literature [39]. In addition to photoionization, thermospray ionization can also occur in APPI sources currently in use [41].

The applicability of APPI to a series of stabilizers including phenolic antioxidants (Irganox MD1024, Irganox 1081, Irganox 1035, Irganox 3114, Irganox 1010, Irganox 1330, Irganox 1076), a benzophenone-type UV absorber (Chimassorb 81), benzotriazol-type UV absorbers (Tinuvin 234, Tinuvin 326, Tinuvin 327, Tinuvin 328), and organophosphite processing stabilizers (Irgafos 126, Irgafos 38, Irgafos 168) has been studied by Himmelsbach et al. [31] using RP-HPLC with mobile phases of acetonitrile and water. Figure 2 shows the comparison of HPLC with UV detection at 200 nm and detection by APPI/MS of a standard solution of these stabilizers. The chromatogram clearly demonstrates the improvement made with APPI/MS detection in comparison with commonly employed UV detection. The results were also compared with APCI and ESI. Table 1 summarizes the detection limits of HPLC/MS with different ionization techniques. In the case of phenolic antioxidants, negative ionization is generally favored over the positive mode, as can be expected from the presence of phenolic groups in these molecules. Overall, APPI performs better for phenolic antioxidants than does APCI and ESI. Also, the UV

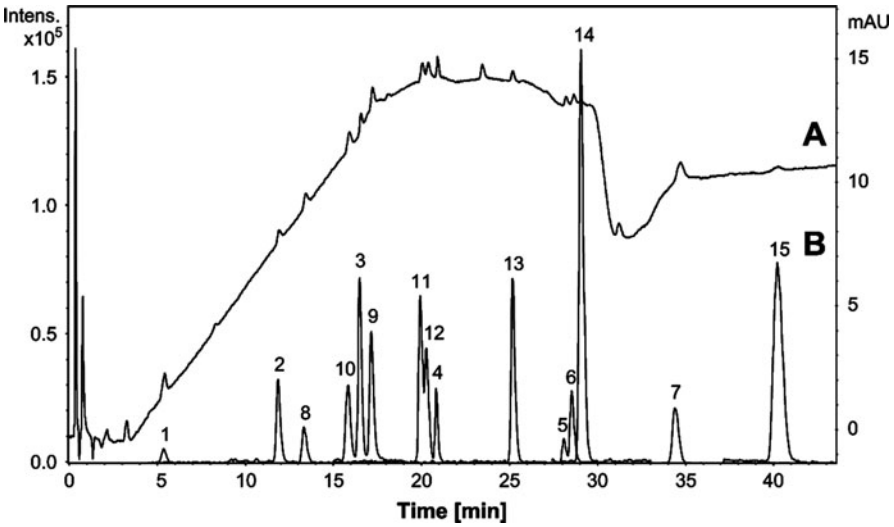

Fig. 2 HPLC separation of stabilizers with UV detection at 200 nm (*A*) and an APPI/MS extracted ion chromatogram (*B*) of a standard solution containing 0.07 mg L^{-1} of each analyte. Peaks: *1* Irganox MD1024, *2* Irganox 1081, *3* Irganox 1035, *4* Irganox 3114, *5* Irganox 1010, *6* Irganox 1330, *7* Irganox 1076, *8* Chimassorb 81, *9* Tinuvin 234, *10* Tinuvin 326, *11* Tinuvin 327, *12* Tinuvin 328, *13* Irgafos 126, *14* Irgafos 38, *15* Irgafos 168. Reprinted from [31] with permission from Elsevier

Table 1 Detection limits (mg L^{-1}) of polymer stabilizers in RP-HPLC/MS using a methanol/water gradient elution with different ionization techniques (data taken from [31])

Analyte	APPI positive	APPI positive with dopant toluene	APPI negative	APPI negative with dopant toluene	APCI positive	APCI negative	ESI positive with formic acid	ESI negative with ammonia
Irganox MD 1024	0.100	0.038	0.022	0.010	0.100	0.040	0.004	0.033
Irganox 1081	0.078	0.700	0.009	0.035	0.900	0.021	0.180	0.011
Irganox 1035	0.008	0.039	0.001	0.002	0.057	0.018	0.003	0.002
Irganox 3114	0.370	1.300	0.007	0.033	0.200	0.067	0.240	0.023
Irganox 1010	0.035	0.030	0.012	0.065	0.032	0.110	0.400	0.022
Irganox 1330	0.013	0.077	0.009	0.009	0.045	0.027	0.049	0.300
Irganox 1076	>10	>10	0.002	0.029	>10	0.015	>10	0.017
Chimassorb 81	0.019	0.060	0.014	0.069	0.290	0.022	0.060	0.038
Tinuvin 234	0.001	0.009	0.001	0.015	0.016	0.011	0.060	0.090
Tinuvin 326	0.100	0.560	0.011	0.110	0.310	0.030	0.070	0.072
Tinuvin 327	0.054	0.710	0.005	0.037	0.400	0.068	0.046	0.051
Tinuvin 328	0.006	0.090	0.005	0.054	0.057	0.042	0.043	0.070
Irgafos 126	0.003	0.008	>10	>10	0.013	>10	0.044	>10
Irgafos 38	0.001	0.005	>10	>10	0.010	>10	0.017	>10
Irgafos 168	0.001	0.018	>10	6.000	0.012	>10	0.028	2.100

absorbers showed lower detection limits in the negative ionization mode than in the positive mode, with APPI outperforming the other ionization techniques. Organophosphite compounds can only be analyzed at sufficiently low concentrations in the positive ionization mode, whereby protonated species are generated. Again, APPI yields the lowest detection limits.

In this context, the behavior of Tinuvin 326 and Tinuvin 327 is interesting. The chemical structures of these two stabilizers contain a chlorine atom. When comparing the APPI responses of Tinuvin 326 and 327 with those of structurally analogous Tinuvin 234 or 328 (which do not contain a chlorine atom), it is evident that in the negative mode the detection limits are quite similar, whereas in the positive mode the detection limits of Tinvin 326 and 327 are considerably worse. This behavior is even more pronounced when looking at the response of the analyte instead of the detection limits. From these results it can be concluded that analogous structures may result in quite different ionization efficiencies if an electronegative group is present or absent in the molecule.

As can be seen from Table 1, the use of a dopant does not improve the detection limits on average. Nevertheless, it is interesting to compare the signal intensities (peak areas) for APPI with and without dopant. Table 2 summarizes the signal intensity enhancement factors obtained by dividing the signal intensity by the peak intensity for APPI without dopant. All data in Fig. 2 refer to the results in the negative ionization mode, except for the Irgafos-type stabilizers for which results from the positive ionization mode are used. Toluene as dopant increases signal intensities by up to a factor of 6.6 (but no signal enhancement is achieved for

Table 2 Signal intensity enhancement in APPI resulting from the use of a dopant, relative to APPI without dopant

Analyte	Enhancement factor		
	APPI	APPI with dopant toluene	APPI with dopant acetone
Irganox MD 1024	1.0	4.8	12.9
Irganox 1081	1.0	6.6	21.9
Irganox 1035	1.0	2.1	9.8
Irganox 3114	1.0	2.0	3.9
Irganox 1010	1.0	1.1	6.4
Irganox 1330	1.0	1.5	7.7
Irganox 1076	1.0	2.9	21.5
Chimassorb 81	1.0	5.3	21.3
Tinuvin 234	1.0	2.2	12.3
Tinuvin 326	1.0	6.1	36.4
Tinuvin 327	1.0	3.4	22.1
Tinuvin 328	1.0	5.3	28.6
Irgafos 126	1.0	1.0	3.6
Irgafos 38	1.0	1.0	4.5
Irgafos 168	1.0	1.0	4.1

All data refer to the negative ionization mode except for the Irgafos-type analytes, which were measured in the positive mode (data taken from [31])

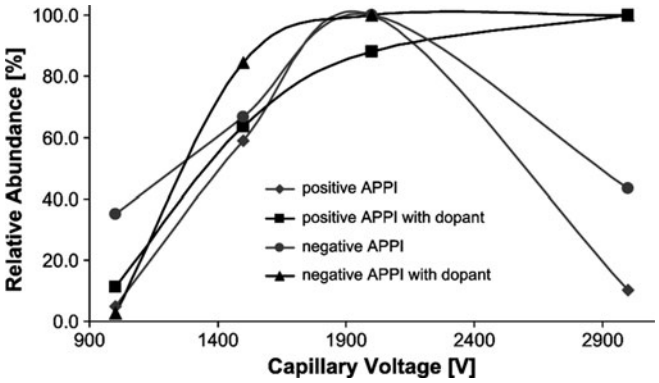

Fig. 3 Effect of MS capillary voltage on the signal intensity of Tinuvin 234 in positive and negative APPI both with and without toluene as dopant. The maximum intensity obtained in each mode is normalized to 100%. Reprinted from [31] with permission from Elsevier

Irgafos-type analytes). Nevertheless, noise also increases so that no significant improvement in the detection limits can be achieved. Even higher enhancement factors of up to 36.4 are observed for acetone as dopant, but again the increasing baseline noise cancels the positive effect of signal enhancement. In this context it is important to be aware of the fact that APPI without or with a dopant may require somewhat different operating parameters, such as the MS capillary voltage. As shown in Fig. 3 for Tinuvin 234, a narrow maximum at about 2,000 V is encountered for the ionization process without a dopant, whereas in case of toluene as dopant a wide range of between 2,000 V and 3,000 V can be used.

3.5 Analysis of Degradation Products of Stabilizers by HPLC/MS

Degradation products of stabilizers can be generated due to oxidative processes and/or heat during processing of the polymeric material, or during use of the material due to environmental impact. Such degradation reactions are typically related to the protection of the polymer by the stabilizer. On the other hand, stabilizers can be degraded by reactions that are not related to their consumption during stabilization, such as by interactions with other additives used in the polymeric material. Whatever the reasons for degradation might be, a decrease in the concentration of intact stabilizer is undesired, and information on the formation of degradation products is required to clarify degradation pathways and to avoid major degradation reactions. On the other hand, HALS stabilizers are recycled during stabilization of the polymer. Therefore, no accumulation of stable degradation products is observed, but intermediate products may occur. Their analysis would be an even more challenging task because their concentrations stay quite low.

Some information about the degradation pathways of stabilizers can be obtained from the results of emission measurements, which are necessary for quality control of polymeric materials with respect to the final application. It is well known that, for example, industrial-grade polypropylene can emit compounds like di-*tert*-butylphenol (the hydrolysis product of phosphite-type stabilizers), *tert*-butylphenol and phenol (generated from di-*tert*-butylphenol), and di-*tert*-butylcresol or di-*tert*-butylbenzoquinone (both generated from phenolic antioxidants). Emission measurements are typically performed by well-established GC methods in combination with MS detection and are not discussed further in this review.

The fragmentation patters observed in mass spectra of pure stabilizers can provide some suggestions about how stabilizers can degrade. Nevertheless, conditions of fragmentation during MS ionization are still significantly different from real-world conditions so that the relevance of MS fragmentation patterns must be critically checked in all cases. Therefore, degradation experiments under controlled conditions must be carried out. A recent review [42] summarizes the degradation products observed so far under controlled conditions. Both GC and HPLC methods have been applied for analysis of degradation products, but HPLC approaches published so far have included MS detection only in a very limited number of cases.

Reingruber et al. [1] have undertaken investigations on the degradation products of pure antioxidants generated under thermal stress, and have extended these studies to mixtures of pure antioxidants and talcum commonly used as inorganic filler in polypropylene. Figure 4 shows the HPLC chromatograms with APPI/MS detection (negative ionization mode) of various stabilizers treated at 115 °C for 24 h in the presence of talcum. The amount of some degradation products generated under these conditions was quite small, but identification of several peaks was still possible. The results of this study are summarized in Table 3. A comparison of APPI with APCI or ESI, showed that APPI is a quite universal detection technique, whereas ESI yielded a much lower number of peaks in the chromatogram.

Besides thermal stress, the impact of chlorinated water on the degradation pathways of stabilizers is of considerable fundamental interest. Various preliminary experiments using HPLC with APPI/MS were carried out by Pan [43]. As an example, the chromatogram of Irganox 1035 after exposure to chlorinated water is given in Fig. 5. During model experiments, this stabilizer underwent quick oxidation at its sulfur atom (besides additional degradation reactions).

4 CE/MS of Additives in Polymers

CE has become a well-established high-performance separation technique that is complementary to liquid chromatography. With respect to the determination of analytes of low to medium molecular weight, capillary zone electrophoresis (CZE) and micellar electrokinetic chromatography (MEKC) as well as microemulsion electrokinetic chromatography (MEEKC) are the most promising techniques. In CZE, the application of a high voltage leads to separation of the analytes due

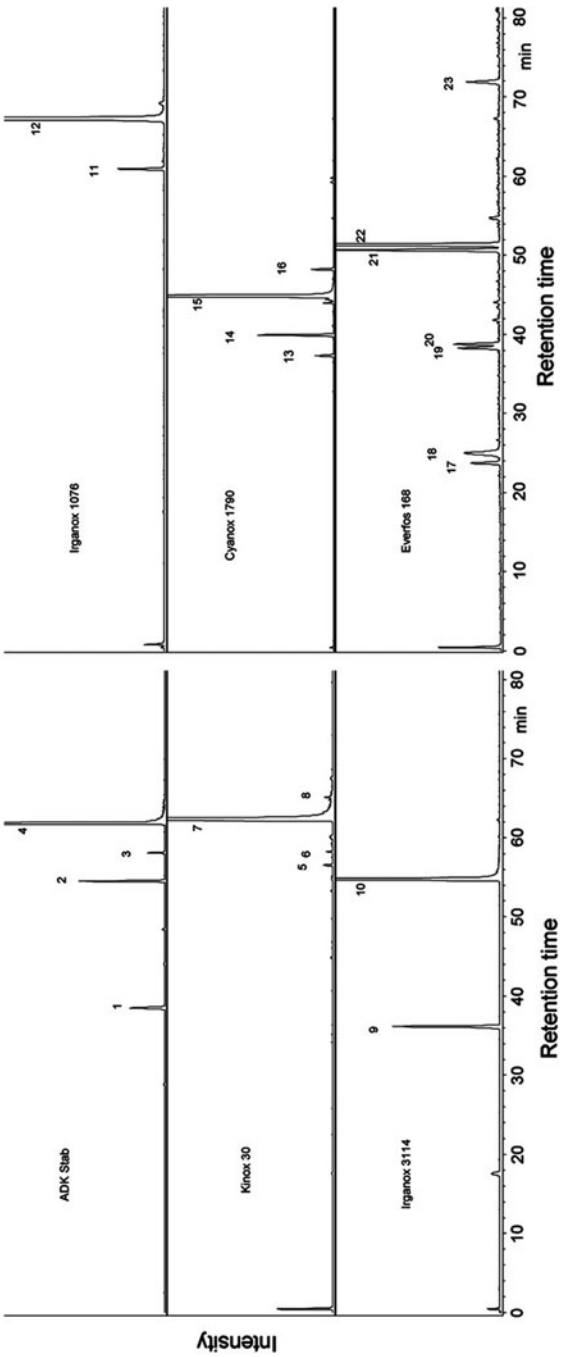

Fig. 4 HPLC-APPI/MS (negative mode) of extracts from model mixtures of different stabilizers with talcum (ADK Stab and Kinox 30 refer to the stabilizers Irganox 1010 and Irganox 1330). Peak numbering see Table 3. Reprinted from [1] with permission from Elsevier

Table 3 Peaks identified in the chromatograms shown in Fig. 4 (adapted from [1])

Peak number	Molecular formula	Identified substances
1	$C_{39}H_{60}O_8$	Irganox 1010, two ester bonds hydrolyzed
2	$C_{56}H_{84}O_{10}$	Irganox 1010, one ester bonds hydrolyzed
3	$C_{69}H_{100}O_{12}$	Irganox 1010, one *tert*-butyl group split off
4	$C_{73}H_{108}O_{12}$	Irganox 1010
5	$C_{39}H_{56}O_2$	Irganox 1330, one di-*tert*-hydroxy-toluene group split off
6	$C_{50}H_{70}O_3$	Irganox 1330, one *tert*-butyl group split off
7	$C_{54}H_{78}O_3$	Irganox 1330
8	$C_{54}H_{76}O_3$	Irganox 1330, one hydroxy group oxidized
9	$C_{33}H_{47}N_3O_5$	Irganox 3114, one di-*tert*-butyl-phenol group split off
10	$C_{33}H_{47}N_3O_5$	Irganox 3114, detected as a fragment with one di-*tert*-butyl-phenol group split off
11	$C_{31}H_{54}O_3$	Irganox 1076, one *tert*-butyl group split off
12	$C_{35}H_{62}O_3$	Irganox 1076
13	$C_{42}H_{57}N_3O_7$	Hydroxylated Cyanox 1790
14	$C_{42}H_{55}N_3O_7$	Oxidized Cyanox 1790
15	$C_{42}H_{57}N_3O_6$	Cyanox 1790
16	$C_{42}H_{57}N_3O_6$	Cyanox 1790 with *tert*-butyl and methyl groups rearranged
17	$C_{14}H_{22}O$	Di-*tert*-butyl-phenol
18	$C_{20}H_{26}O_2$	Reaction product of two mono-*tert*-butyl-phenols
19	$C_{18}H_{30}O$	Tri-*tert*-butyl-phenol
20	$C_{24}H_{34}O_2$	Reaction product of a mono- with a di-*tert*-butyl-phenol
21	$C_{28}H_{43}O_3P$	Irgafos 168, one di-*tert*-butyl-phenol group split off
22	$C_{28}H_{42}O_2$	Reaction product of two di-*tert*-butyl-phenols
23	$C_{28}H_{43}O_4P$	Irgafos 168, detected as an oxidized fragment with one-di-*tert*-butyl-phenol group split off

to migration in a suitable carrier electrolyte according to their electrophoretic mobilities, which depend on their charge/size ratio. Fused silica capillaries generally used in CE provide a negative charge at the inner surface as a result of the dissociation of silanol groups, thereby generating an electroosmotic flow (EOF), also called electroosmotic mobility, that is normally directed towards the cathode and superimposes the electrophoretic mobility of analytes. Therefore, the total mobility of an analyte is the vector sum of the electrophoretic mobility and the electroosmotic mobility.

Besides CZE, CE techniques involving a pseudostationary phase such as micelles or a microemulsion in the carrier electrolyte are frequently applied. If micelles consisting of an anionic surfactant are employed, their electrophoretic mobility will be directed to the anode, whereas the electroosmotic mobility is directed towards the cathode. In the case of an alkaline carrier electrolyte that produces a relatively high EOF, the total mobility of the micelles will be directed towards the cathode but will be smaller than the EOF. A neutral hydrophilic analyte will move with the velocity of the EOF. Hydrophobic analytes will also undergo a partitioning equilibrium with the pseudostationary phase and will move at a lower

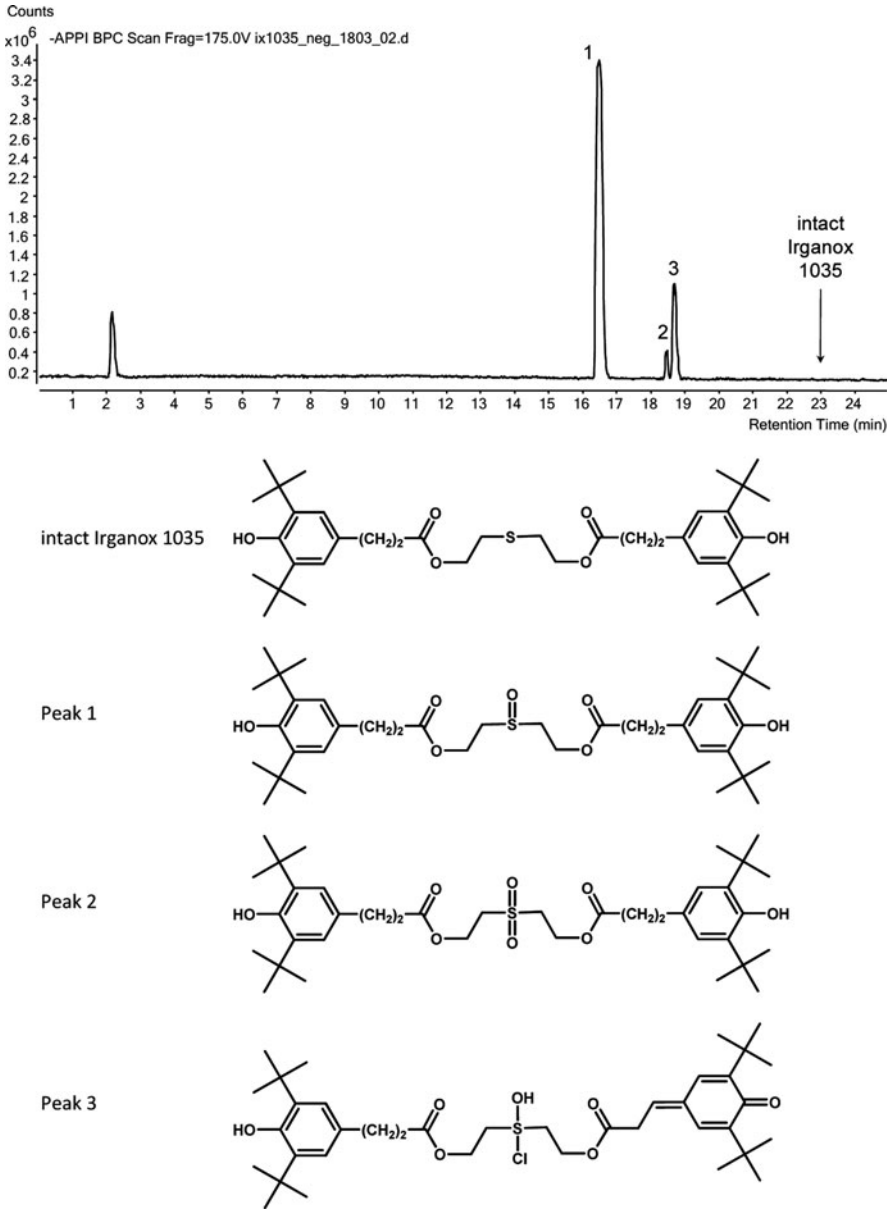

Fig. 5 HPLC-APPI/MS of the stabilizer Irganox 1035 and major degradation products after exposure to chlorinated water (adapted from [43])

speed than hydrophilic analytes. Therefore, a separation of neutral analytes can be achieved on the basis of their hydrophobic properties. Instead of micelles in MEKC, a microemulsion (tiny droplets of a solvent such as octane that is not miscible with

water) stabilized by dodecylsulfate ions that attach to the surface of the droplets and result in a negative charge can be used as the pseudostationary phase (MEEKC).

Regarding CZE for separation of additives for polymers, there are few applications up to now. This is mostly the result of a lack of sufficiently ionizable groups as well as of problems with solubility in carrier electrolytes suitable for CZE. Some preliminary work has been carried out for separation of HALS [18] using a carrier electrolyte of phosphoric acid in methanol, but a fully satisfactory separation of different stabilizers has not yet been achieved.

MEEKC has turned out to be much more promising for separation of hydrophobic polymer additives such as various phenolic antioxidants (Irganox 1024, Irganox 1035, Irganox 1076, Irganox 1010, Irganox 1330, Irgafos 138, Irganox 168, 2,6-di-*tert*.-butyl-4-methylphenol) [44]. The optimized carrier electrolyte consisted of 2.25% (w/w) sodium dodecylsulfate (SDS), 0.75% (w/w) Brij 35, 0.8% (w/w) n-octane, 6.6% (w/w) 1-butanol, 25% (w/w) 2-propanol, and 64.6% (w/w) 10 mM borate buffer (pH 9.2). The addition of 2-propanol was done to manipulate the partitioning of analytes between the borate buffer and the pseudostationary phase. The use of two different surfactants, the anionic SDS and the neutral Brij 35, allowed sufficient stabilization of the microemulsion. Changing the ratio of the two surfactants allowed the manipulation of the charge of the droplets and thereby their velocity. A typical separation of the phenolic antioxidants is shown in Fig. 6.

Nowadays, CE can be combined with MS detection, yielding an instrumentation that is not only suitable for research but can also be used in routine analysis. In this context, a few aspects must be taken into account. Commercially available ESI, APCI, or APPI sources (typically designed for combination with HPLC) require flow rates that are considerably higher than the flow rates in CE. In addition, at the end of the separation capillary the current from the electrophoretic separation has to

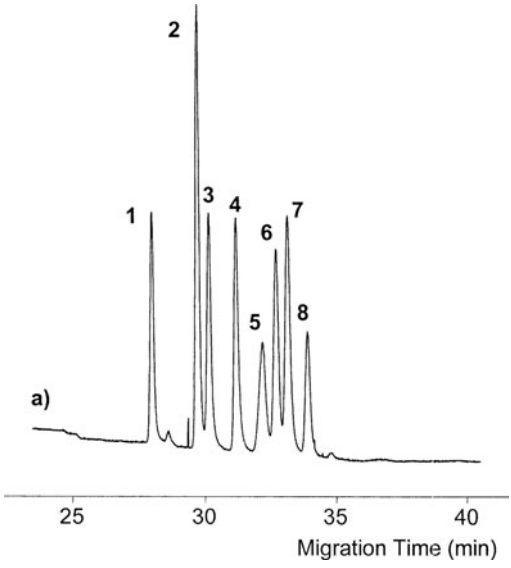

Fig. 6 Separation of stabilizers by MEEKC. Peaks: *1* Irganox 1024, *2* 2,6-di-*tert*-butyl-4-methylphenol, *3* Irganox 1035, *4* Irgafos 38, *5* Irgafos 168, *6* Irganox 1010, *7* Irganox 1330, *8* Irganox 1076. Reprinted from [44] with permission from Elsevier

be grounded and, in the case of ESI, the spray potential must also be applied. For these reasons, the most widely used design for combination of CE with MS is the sheath liquid interface, which is based on a make-up flow at the end of the capillary. Electrical contact is made via the make-up flow.

Another problem encountered for combination of CE and MS is the limited compatibility of components of the carrier electrolyte with the ionization process. ESI in particular can suffer considerably when operated with carrier electrolytes containing less volatile electrolytes. In MEEKC, the carrier electrolytes containing pseudostationary phases are often considered incompatible with ESI. On the other hand, recent work has demonstrated that combination of CE with APPI/MS can avoid a major loss of performance [45].

Up to now, there have been hardly any papers dealing with CE and MS detection for analysis of additives in polymeric materials. Nevertheless, an example of the successful implementation of CE/MS in polymer analysis is the determination of reaction products from the condensation of melamine (M) with formaldehyde (F) in M–F resins. Although this application does not deal with typical additives in polymers, it is a good example of the application of CE/MS for characterization of polymers with respect to their varying properties, and is therefore included here. M–F condensation products such as MF, MF_2, MF_3,... and M_2, M_2F, M_2F_2, M_2F_3,... become protonated under acidic conditions and are efficiently separated in a formic acid-based carrier electrolyte containing 50% acetonitrile. The use of a TOF/MS detector allows the assignment of molecular structures [46]. As can be seen from Fig. 7, even isomers can be separated using CZE.

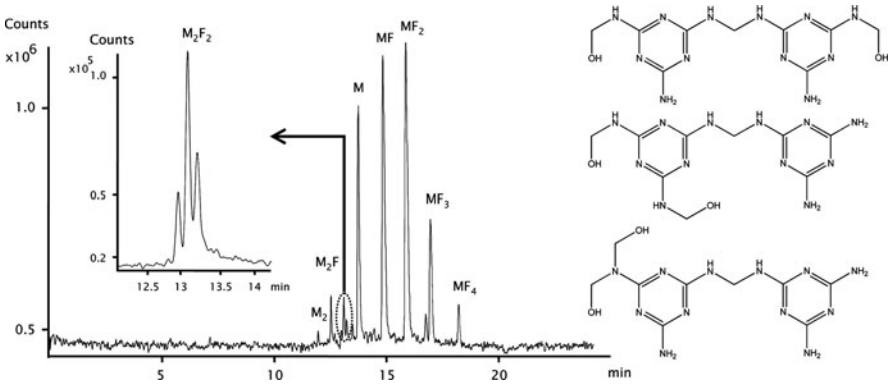

Fig. 7 CZE/MS electropherogram of a melamine (M)/formaldehyde (F) resin showing different reaction products from the condensation of M with F. The *inset* shows the separated isomers of M_2F_2 for which the chemical structures are given on the *right*. Reprinted from [46] with permission from Elsevier

5 Combination of Liquid Chromatography and Pyrolysis-GC/MS

Nowadays, pyrolysis-GC/MS is a routine tool in polymer analysis for identification of the polymer itself as well as for determination of additives that are not sufficiently volatile to be analyzed in their intact forms. Unfortunately, peaks resulting from the polymer may seriously interfere with peaks from additives present at low levels. Furthermore, structurally related additives may yield the same pyrolysis products so that pyrolysis-GC/MS would not be able to differentiate between them. In such cases, the on-line combination of a liquid chromatographic technique with pyrolysis-GC/MS would be an interesting alternative. In such an approach, pyrolysis-GC/MS would act as "detector" for the liquid chromatographic separation. Possible realizations of the combination of liquid chromatography with GC via a programmed temperature vaporizer for elimination of the solvent have been reported various times and have served as the basis for the work of Kaal et al. [47] who demonstrated on-line SEC coupled with pyrolysis-GC/MS for simultaneous polymer characterization and additive analysis. Figure 8 shows the chromatograms for the analysis of polycarbonate containing two additives, Irganox 1076 and Irganox 3114. Two fractions of the polymer peak of the SEC separation were transferred to pyrolysis-GC/MS and showed bisphenol-A as the main peak. Fractions of the later eluting peak containing low molecular weight stabilizers

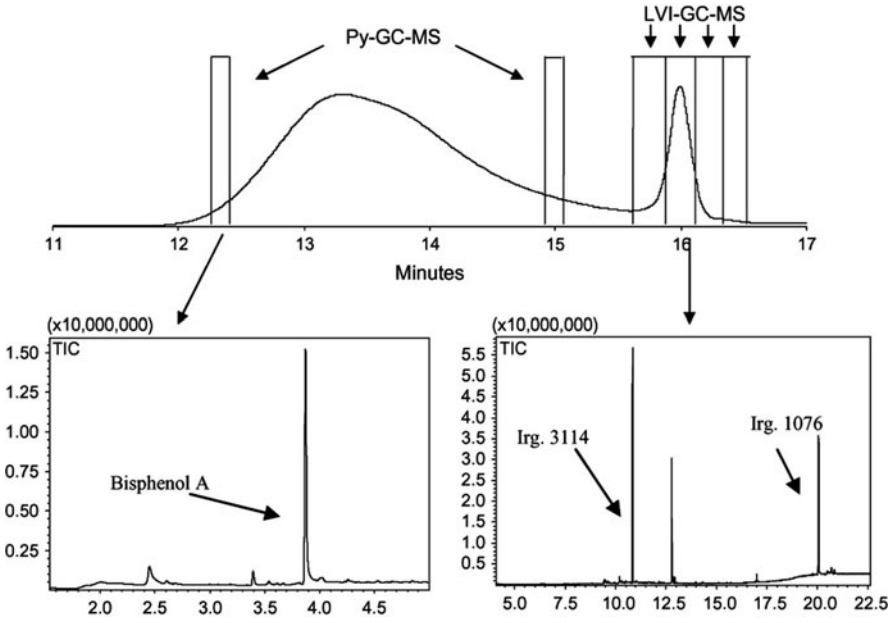

Fig. 8 Simultaneous polymer characterization and additive analysis of a polycarbonate sample using SEC coupled to pyrolysis-GC/MS. *TIC* total ion chromatogram. Reprinted from [47] with permission from Elsevier

were transferred in a similar way and yielded MS signals that allowed a clear identification. Depending on the analytes, the GC injector can operate as simple large-volume injector (LVI) for analytes that are sufficiently volatile, or as pyrolysis injector for nonvolatile analytes. Furthermore, this technique is not restricted to a combination with SEC as liquid chromatographic technique because other techniques like RP or NP chromatography will work as well. Thus, one may think of a range of applications not yet investigated in the area of additive analysis.

6 Direct Mass Spectrometry for Determination of Additives in Polymers

As mentioned in the Introduction, most currently used routine techniques for determination of additives in polymers require dissolution of the polymer for the extraction of analytes from the polymer. These steps may be quite time-consuming and therefore not fully compatible with the requirements of rapid screening procedures. Some alternatives based on novel MS techniques suitable for solid polymer samples have been introduced recently. Some of the approaches are briefly summarized below. They may deliver semiquantitative information rather than quantitative results, but nevertheless they can be very suitable for screening of unknown samples prior to HPLC analysis. It should be made clear that such direct MS measurements give information about additives present in the surface layer of the solid sample, therefore the results may be different from bulk analysis achieved by traditional HPLC analysis after dissolution or extraction of the sample.

6.1 Desorption Electrospray Ionization/Mass Spectrometry

Desorption electrospray ionization (DESI) was developed by Cooks and coworkers [48]. It is based on the flow of a liquid that is converted into an electrospray by applying a high voltage. The charged droplets are directed to the surface of the solid sample under atmospheric pressure. A possible mechanism suggested for the ionization process consists of the impact of the charged droplets on the sample, whereby the analyte is dissolved into the droplets. Subsequently, secondary droplets containing analyte molecules are ejected from the surface and move to the mass analyzer under conditions similar to conventional ESI.

DESI has recently been applied to a set of light stabilizers including Chimassorb 81 (a benzephenone derivative), Tinuvin 326 and 328 (benzotriazole derivatives), and Tinuvin 770 (a sterically hindered amine) in polypropylene samples [49]. These investigations indicated that best results can be achieved with a spray solution of methanol/water/formic acid (80/20/0.1). Calibration curves obtained with polymer samples containing the stabilizers at concentrations of 0.02, 0.05, 0.1, and 0.2% (w/w) yielded satisfactory linearity and values for R^2 better than 0.994. Figure 9

shows the mass spectra of a model polymer sample containing all four additives at a concentration of 0.2% (w/w), of a vinyl liner for an in-ground swimming pool, and of technical polypropylene granules.

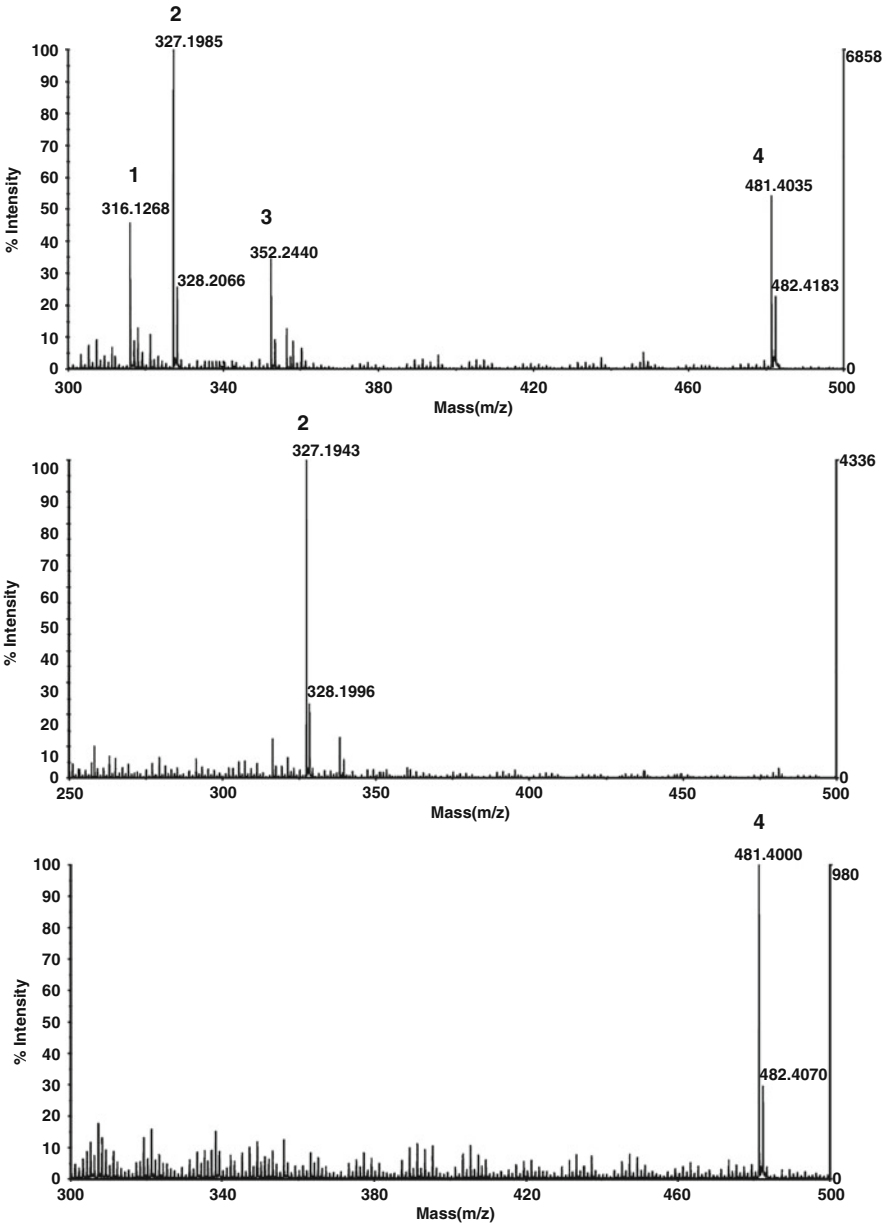

Fig. 9 DESI/MS of (**a**) model sample containing four stabilizers at a concentration level of 0.2%, (**b**) vinyl liner for a swimming pool, and (**c**) technical polymer granule. Analytes: *1* Tinuvin 326, *2* Chimassorb 81, *3* Tinuvin 328, *4* Tinuvin 770. Reprinted from [49] with permission from Springer

6.2 Direct Analysis in Real Time/Mass Spectrometry

The direct analysis in real time (DART) ion source was developed by Cody and Laramee and details were first published in 2005 [50]. Since then, this ion source has become commercially available and consists of a tube of several chambers through which a gas like helium flows. In the first chamber, a glow discharge is generated and produces ions, electrons, and excited state atoms (metastable species) such as $He(2^3S)$. In the second chamber, an applied voltage removes charged species, and only excited state species flow to a third chamber, which can be heated. Afterwards, the excited state species interact with the sample such as a solid polymer (samples in the liquid state can be analyzed as well) at atmospheric pressure to produce and desorb ionized analyte species that are directed to the inlet of the mass analyzer operating under high vacuum.

Ionization of the analyte A by $He(2^3S)$ may occur through Penning ionization:

$$He(2^3S) + A \rightarrow A^+ + He(^1S) + e^-$$

More important may be the following reaction between $He(2^3S)$ and atmospheric moisture, leading to protonated water clusters:

$$He(2^3S) + nH_2O \rightarrow [(H_2O)_{n-1} + H]^+ + OH^- + He(1^1S)$$

These protonated water clusters may ionize the analyte A by proton transfer:

$$[(H_2O)_n + H]^+ + A \rightarrow [A + H]^+ + nH_2O$$

Ammonium adducts $[A+NH_4]^+$ may be observed if ammonia is introduced into the sample region. In addition to the formation of positively charged ions, DART may also generate negatively charged ions, although the relevant mechanisms have not yet been fully investigated.

Recently, Haunschmidt et al. [51] systematically investigated the ionization by DART of various stabilizers. All analytes could be measured in the positive mode as $[A+H^+]$, as A^+, or as $[M+NH_4]^+$ and several could also be measured in the negative mode, yielding $[M-H]^-$ or $[M+O_2]^-$ ions. Generally, the positive mode proved to provide better sensitivities. The applicability to solid polymer samples was tested using laboratory-made polypropylene samples containing various sets of stabilizers. DART also allowed the identification of decomposition products of stabilizers generated due to the elevated temperature of the compounding process. In Fig. 10, the mass spectrum of a polymer sample containing Irgafos 126 and degradation products after compounding at 190 °C is given (to avoid misunderstanding, it is important to mention that the various signals in the mass spectrum do not represent fragment ions generated during the ionization process

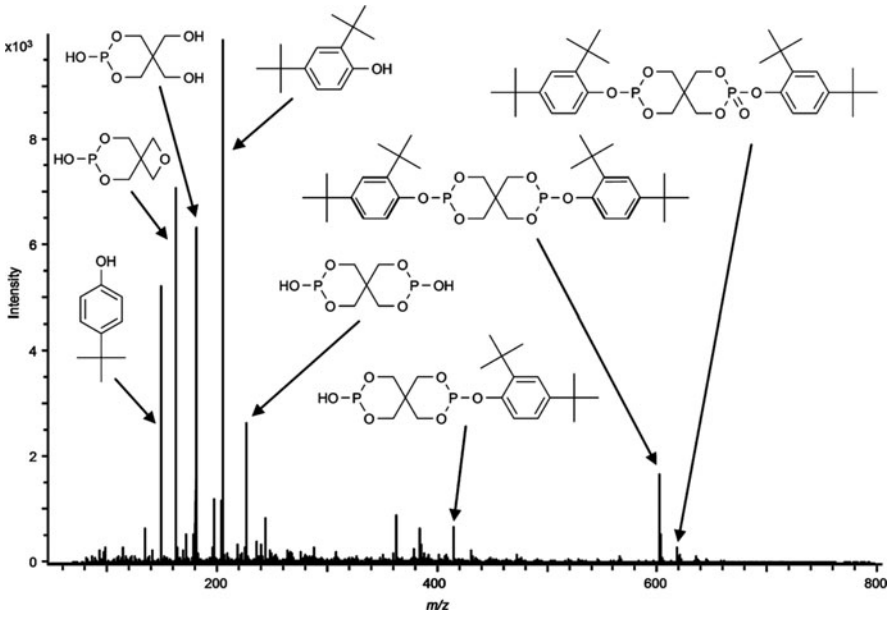

Fig. 10 DART/MS spectrum of a polymer sample containing Irgafos 126 and degradation products after compounding at 190 °C. Reprinted from [51] with permission from The Royal Society of Chemistry

but are indeed caused by degradation of the stabilizer during the compounding process).

It is fair to say that DART/MS of solid polymer samples often delivers semi-quantitative results rather than quantitative results and is most suitable for a quick qualitative screening for the presence of stabilizers in a polymer sample. On the other hand, it has recently been demonstrated that DART is not only suitable for solid sample analysis but can also be used as an MS detection technique for HPLC [52]. In this case, the eluent is not sprayed and vaporized but a liquid jet is formed from which the analytes are ionized by the DART mechanism. Although applications of HPLC-DART to polymer additives have not yet been reported, it could be an attractive additional tool within the range of MS detectors.

6.3 Atmospheric Solid Analysis Probe Technique

The atmospheric solid analysis probe (ASAP) technique is based on an APCI ionization mode. As this mode is widely applicable in polymer additive analysis (see Sect. 3.3), ASAP may be very suitable for use in this area. It uses a traditional APCI source, where the solid sample is positioned into the hot nitrogen gas flowing from the probe, thereby allowing the ionization of analytes by the corona discharge.

The direct qualitative analysis of erucamide, Irganox 1076, Irgafos 168, Irganox 3114, and several brominated flame retardants has been demonstrated by Trimpin et al. [53].

6.4 Other Approaches

Secondary ion mass spectrometry (SIMS) has been investigated for direct analysis of additives in solid samples (see for example the review in [54]) but a detailed discussion would be beyond the scope of this paper.

Last but not least, the potential of solvent-free matrix-assisted laser desorption/ionization (MALDI) MS has been explored by Trimpin et al. [53] using pre-ground solid mixtures of matrix and sample. Applications so far reported refer to identification of the polymer itself, but the determination of additives should be possible as well.

7 Conclusions

Currently, a range of different chromatographic techniques is available for quantitative analysis of additives and stabilizers in polymeric materials. MS detection has become state-of-the-art for GC, where electron ionization and chemical ionization provide an almost universal ionization of analytes from applications in polymer analysis. Unfortunately, many additives or stabilizers commonly used are not suitable for GC analysis due to insufficient volatility. Therefore, techniques operating in the liquid phase such as HPLC have attained significant importance for separation of various different stabilizers or additives within one run. HPLC has become even more attractive within the last few years due to the availability of highly efficient columns with stationary phases consisting of particles sizes below 2 μm. These stationary phases have increased the peak capacity (number of peaks that can be separated within a certain time window) tremendously and their importance will continue to rise in the near future. Nowadays, atmospheric pressure ionization modes are well established for MS detection in HPLC. Although the applicability is not as universal as ionization sources for GC, some more recent developments like photoionization have resulted in efficient ionization tools for a wide range of structurally different additives and their degradation products in polymers. The increasing availability of reasonably priced high-resolution TOF/MS analyzers allowing exact mass determination as well as the development of MS/MS instruments such as quadrupole-TOF or ion trap-TOF make structure elucidation of unknown peaks in non-target analysis quite simple. Detection limits of MS detection are considerably better than for commonly employed UV detectors and will undergo further improvements in the future due to ongoing instrumental developments in MS.

HPLC methods published so far have demonstrated the separation of structurally different additives or stabilizers within a single run. On the other hand, routinely employed methods are often still optimized just for a certain class of analytes so that different HPLC procedures are used side by side to cover the whole range of stabilizers or additives possibly present in real samples. The development of more universal and fully MS-compatible HPLC conditions may be a major challenge in the near future.

A bottleneck for HPLC/MS analysis of additives in polymers may still be the sample preparation step, which can be quite time-consuming and labor-intensive. Furthermore, it can be difficult to prove that extraction of analytes from real samples is quantitative. It is not surprising that direct MS methods for solid polymeric materials are the focus of current research. New ion sources such as DART have become commercially available and complement traditional ion sources for solid samples like MALDI. Some efforts will still be necessary to allow fully quantitative measurements by such direct techniques.

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