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**Direct Detection of Additives and Degradation Products from Polymers by Liquid
Extraction Surface Analysis Employing Chip-Based Nanospray Mass Spectrometry**

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Abstract

Rationale: Polymer-based surface coatings in outdoor applications experience accelerated degradation due to exposure to solar radiation, oxygen and atmospheric pollutants. These deleterious agents cause undesirable changes to the polymers aesthetic and mechanical properties reducing its lifetime. The use of antioxidants such as hindered amine light stabilisers (HALS) retard these degradative processes, however, mechanisms for HALS action and polymer degradation are poorly understood.

Methods: Detection of the hindered amine light stabiliser (HALS) TINUVIN[®] 123 (bis (1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl) sebacate) and the polymer degradation products directly from a polyester-based coil coating was achieved by liquid extraction surface analysis (LESA) coupled to a triple quadrupole QTRAP[®] 5500 mass spectrometer. The detection of TINUVIN[®] 123 and melamine was confirmed by the characteristic fragmentation pattern observed in LESA-MS/MS spectra that was identical to that reported for authentic samples.

Results: Analysis of an unstabilised coil coating by LESA-MS after exposure to four years of outdoor field testing revealed the presence of melamine (1,3,5-triazine-2,4,6-triamine) as a polymer degradation product at elevated levels. Changes to the coil coatings physical appearance including powder-like deposits on the coatings surface were observed to coincide with melamine deposits and are indicative of the phenomenon known as polymer ‘blooming’.

Conclusions: For the first time, *in situ* detection from a thermoset polymer coating was accomplished without any sample preparation providing advantages over traditional extraction-analysis approaches and some contemporary ambient MS methods. Detection of HALS and polymer degradation products such as melamine provide insight into the mechanisms by which degradation occurs and suggests LESA-MS is a powerful new tool for polymer analysis.

Introduction

Coil coating is a cost-effective and efficient method of applying polymer-based coatings to pre-finished metal products in large scale industrial applications.^[1] This continuous strip coating approach where rolled sheets of metals are continuously coated provides a simpler, more robust method than painting the complex shapes of finished products (*e.g.*, automotive manufacture).^[2] Over 70 % of these pre-painted metal products are used in exterior construction applications (*e.g.*, roofing) and are therefore highly susceptible to degradation or “weathering” through thermal and photo-oxidative processes; being exposed to high temperatures in the presence of ultraviolet (UV) radiation, humidity and oxygen for extended periods of time.^[2, 3] Weathering of coil coatings in this manner produce degradation products that are concentrated at or near the surface of the material. The location and low concentration of such products can be difficult to detect by conventional methods, but their characterisation is essential in order to address questions about the stability of the materials and mechanisms of their degradation. Under some circumstances degradation products concentrating at the surface can also adversely affect the aesthetic qualities of the polymeric material. For example, the effect known as “blooming” describes the appearance of a polymer with powder-like deposits or crystals forming on its surface. There are many different causes of blooming but often results from partial dissolving and redepositing of pigment or other polymer components by a solvent onto the surface.^[4]

Different types of additives (such as UV absorbers or antioxidants) can be used to retard the degradation caused by exposure to heat and UV light and are typically added during the coatings formulation at low concentrations.^[5-7] Hindered amine light stabilisers

(HALS) represent a sub-class of antioxidants used to retard degradation and are present in many plastic and coating applications; recently finding their way into coil coatings. HALS operate as chain-breaking antioxidants whereby, initially, the parent compound undergoes sacrificial oxidation of a heterocyclic amine to a nitroxyl radical.^[8] It is this persistent nitroxyl radical that acts as a free radical scavenging intermediate and is thought to be involved in converting harmful propagating free radicals generated *in situ* to less harmful even-electron species.^[8] In theory, this process can repeat indefinitely although HALS are known to be modified and lost over time prompting a recent review of their mechanism of action.^[9, 10]

The detection and characterisation of HALS within polymer-based surface coatings has received some interest of late, as the performance and chemical activity of HALS *in situ* can have dramatic effects on plastic and coating performance over the lifetime of the material.^[11-15] Many different analytical techniques have been used for direct detection of HALS from polymer-based materials, the most notable being ambient mass spectrometry (MS) techniques such as atmospheric pressure – matrix assisted laser desorption ionisation (AP-MALDI) and desorption electrospray ionisation (DESI-MS).^[16-18] These techniques allow direct detection of analytes from the surface of the material without the need to extract samples into a solution or the gas phase prior to analysis. Coupled with mass spectrometry these approaches provide rich qualitative and quantitative information, however, both require some degree of sample preparation, *i.e.*, matrix deposition for MALDI^[16-18] or swelling of the polymer with solvent in the case of DESI.^[9] These requirements complicate the process and extend the analysis time.

Ambient surface analysis can also be achieved via direct liquid extraction techniques including the recently developed liquid extraction surface analysis (LESA).^[19] This technique is now commercially available via adaption of a robotic pipette tip system that allows the formation of a liquid-surface microjunction between the pipette tip and the sample. The microjunction created allows extraction of analyte into a small volume of solvent before being aspirated back into the pipette tip for introduction to the mass analyser via a chip-based infusion nanoESI system.^[20] LESA has been implemented for the analysis of spotted MALDI target plates, dried blood spots on paper, porcine ear tissue sections and food surfaces.^[19-22] Creating this microjunction can be difficult on wettable or absorbent surfaces and works best on flat, homogeneous and hydrophobic surfaces that facilitate the stabilisation of liquid microjunctions making it ideal for coil coating analysis.

In this paper, LESA-MS analysis of a polyester-based thermoset coil coating formulated with a commercially available HALS is reported and reveals direct detection of this species from the coatings surface without pre-treatment. LESA-MS was also applied to a coil coating with no stabiliser present with samples analysed after exposure to field-testing designed to simulate roofing applications.

Methods

Reagents

Methanol and formic acid were HPLC grade (Crown Scientific, Minto NSW, Australia). Chloroform was analytical reagent (AR) grade (Crown Scientific, Minto NSW, Australia). TINUVIN[®] 123 (bis (1-octyloxy-2,2,6,6-tetramethyl-4-piperidiny) sebacate) was supplied by Ciba Specialty Chemicals (Basel, Switzerland) and was used without purification.

Preparation of coated steel samples

The paint system employed in these studies was a solvent-borne, polyester topcoat paint incorporating a melamine-formaldehyde cross-linker, acid catalysed and formulated for coil paint-line application. As a wet paint, this sample was found to be 40% w/w resin solids by thermogravimetry (Perkin-Elmer TGA 7, Perkin-Elmer Co. Ltd., Norwalk CT, USA). Where HALS have been added, a bulk sample of this paint was sub-sampled and weighed into small containers with TIN123 added at *ca.* 2% (based upon total resin solids). In a typical formulation a subsample of paint weighed 49.61 g, equating to a total resin solids content of 19.84 g. To this sample 0.413 g of TIN123 was added giving 2.08% on a total resin solids basis. The coated samples were laboratory prepared upon pre-primed (commercial chromated polyester primer) panels of a 0.6 mm thick GALVALUME[®]-type steel substrate. Wet paint was applied using a #28 wire-wound draw-down bar then cured for 55 seconds in a fan forced oven set at 262 °C. Under these conditions, 55 seconds equates to a peak metal temperature of 232 °C.

Weathering of cured paint samples

Cured polyester-based surface coatings were exposed to varying amounts of either artificial or natural weathering conditions. Artificial weathering was carried out in-house with a Q-Sun xenon test chamber (Q-Lab Corporation, Westlake OH, USA) that utilises a xenon arc lamp to mimic the full solar spectrum. The coatings were exposed for 900 hours continuous cycle of 8 hours of xenon arc light at 80 °C followed by 4 hours of darkness at 50 °C. Field testing designed to simulate natural weathering conditions experienced by polymer-based surface coatings in roofing applications was also carried out at a testing site (Rockhampton, QLD). Coated steel samples were exposed for a period of four years.

Liquid Extraction Surface Analysis Mass Spectrometry (LESA-MS)

Metal panels with a thermosetting polyester-based coating were cut into small sections (25 x 75 mm) using hydraulic shears and placed in the LESA sample holder. Positive ion LESA-MS spectra were acquired using TriVersa NanoMate[®] (Advion, Ithaca NY, USA) coupled to a triple quadrupole QTRAP[®] 5500 mass spectrometer (AB Sciex, Foster City CA, USA) with Analyst[®] 1.5.1 software (AB Sciex, California, USA) used for spectral acquisition. Typical LESA-MS experimental conditions were spray voltage (1.4 kV), N₂ delivery gas (0.3 psi) and MeOH:CHCl₃ (2:1) with 0.1 % formic acid (v/v) as the solvent system. A total volume of 2 µL of this solution was used for each experiment with 1 µL being dispensed 0.6 mm above the surface by the automated pipette tip, forming a liquid-surface junction facilitating liquid extraction of analytes. The liquid junction was held in

place for 1 second before being aspirated back into the pipette tip. This process was repeated three times using the same volume of solvent to maximise analyte concentration in the aspirated solvent prior to analysis. Positive ion LESA-MS/MS spectra were acquired on the QTRAP[®] 5500 by subjecting mass filtered ions using the experimental conditions above to collision-induced dissociation (CID). Typical experimental parameters for CID experiments include normalised CID energy (25-30 arb), declustering potential (100 V), entrance potential (10 V), exit potential (2 V) and scan rate (200 m/z units.s⁻¹). Baseline subtraction was not used and mass spectra were averaged over a minimum of fifty scans. All mass spectra were normalised to the most abundant ion in the spectrum.

Results & Discussion

Stabilised Coil Coating

Positive-ion LESA-MS spectra were acquired directly from cured polyester-based coil coatings formulated with the HALS TINUVIN[®] 123. Spectra were measured from both control panels (Figure 1a) prior to UV light or heat exposure and samples subjected to following 900 hours within a Q-Sun xenon test chamber (Figure 1b). These data were obtained using a methanol:chloroform (2:1 ratio) solution acidified with formic acid (0.1 % v/v). This solvent composition was optimised to achieve: (i) a stable liquid microjunction between the solvent droplet and the polyester surface, (ii) sufficient swelling of the polymer substrate to extract HALS into the solvent, and (iii) the ability to generate a stable ion current from the electrospray source. Methanol is present as the major component in order to maintain a stable electrospray while the use of chloroform swells the polymer and facilitates extraction of the HALS into the solvent mixture. For positive-ion mode ESI-MS, formic acid is also added to the solvent at low concentrations to aid protonation of the analyte, increasing the abundance of ions for detection.

Figure 1(a) exhibits two major peaks at m/z 369.4 and 737.6 that correspond to the $[M+2H]^{2+}$ and $[M+H]^+$ ions of TIN123 respectively. The assignment of these ions was confirmed by the characteristic fragmentation patterns arising from CID of the m/z 369.4 (Figure 1c) and m/z 737.6 (data not shown) precursor ions. The resulting product ions from the LESA-MS/MS spectrum (Figure 1c) are consistent with those previously reported from analysis of authentic TIN123 in solution by electrospray ionisation mass spectrometry (ESI-MS) and desorption electrospray ionisation mass spectrometric (DESI-MS) analysis of an identical coating.^[9, 23] Excellent reproducibility was observed for the

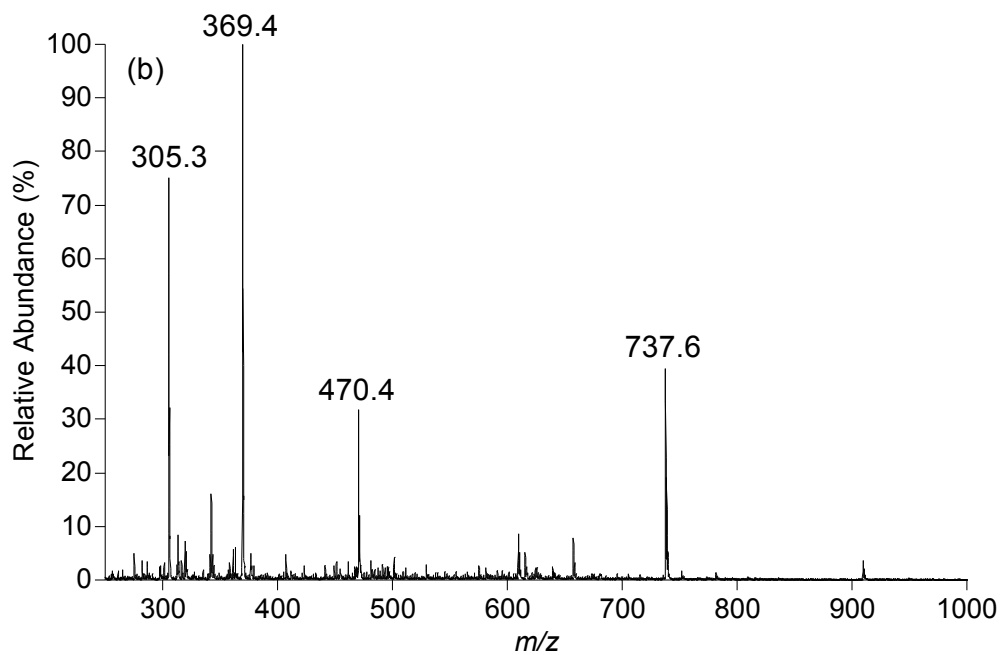
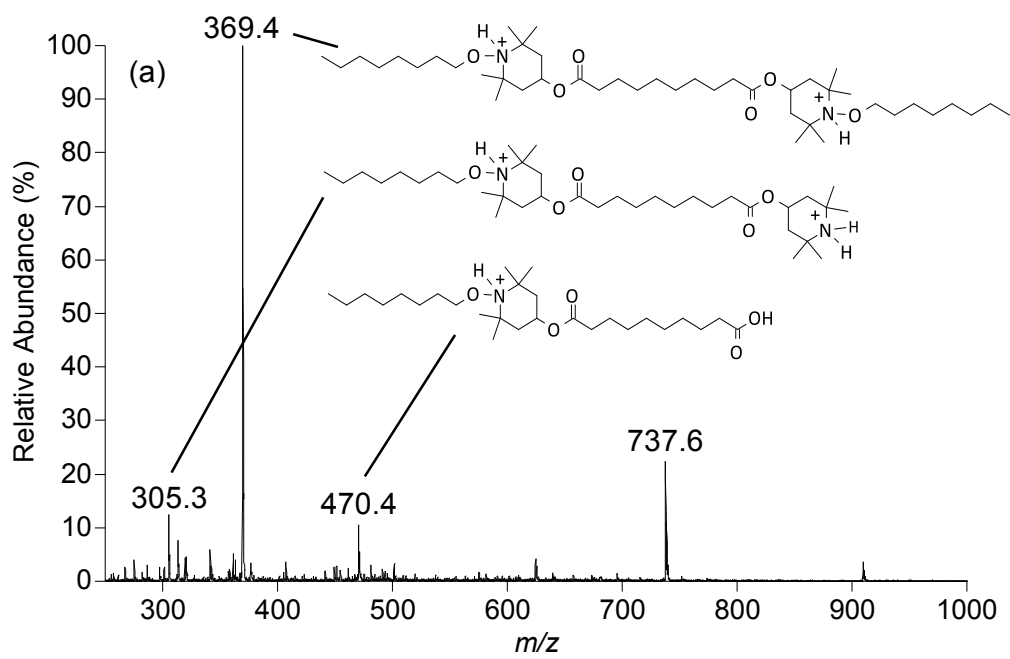
LESA-MS analysis with analyses of up to seven different spots on the same panel giving ion counts for the $[M+H]^+$ ion with a coefficient of variance of better than 5%.

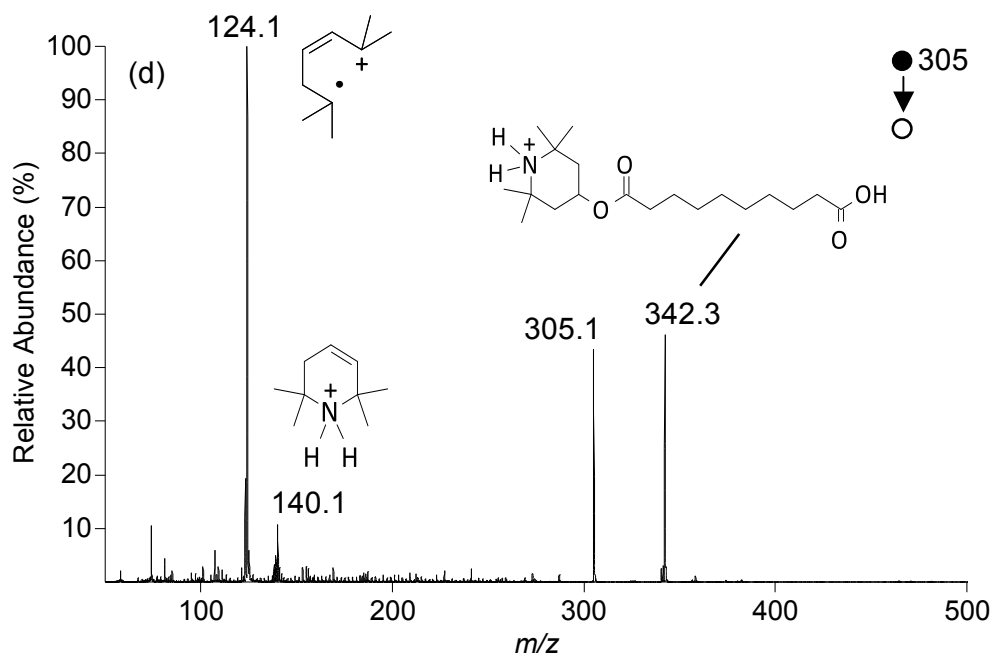
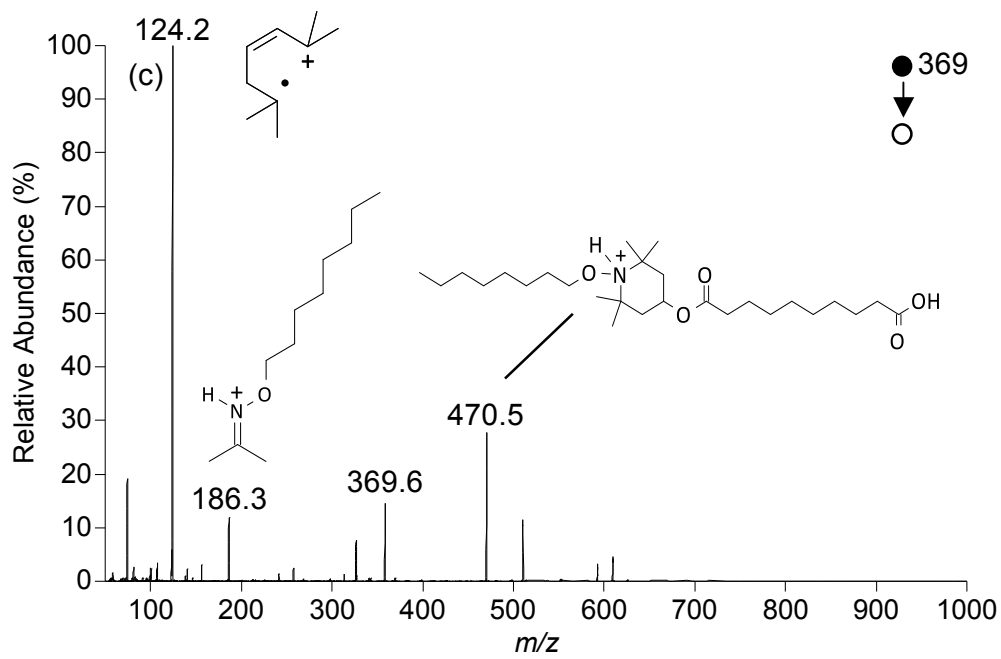
Figure 1(a) also exhibits two minor peaks at m/z 305.3 and 470.4 that are detected in the cured coating at low abundances. Upon exposure of an identical coating to accelerated weathering (*i.e.* elevated levels of UV light and heat), the relative abundance of these two minor peaks increases with respect to the signal observed for the parent TIN123 compound (Figure 1b).

The ion at m/z 305.3 has been identified in a previous study as an *in situ* degradation product of TIN123 (1-octyloxy-bis-(2,2,6,6-tetramethyl-4-piperidyl) sebacate; Figure 1a – inset) and represents the $[M+2H]^{2+}$ ion of TIN123 after the loss of one alkylether group from a piperidinyl nitrogen followed by addition of a hydrogen atom.^[9] The structural assignment of this degradation product is further supported by the characteristic fragmentation pattern observed for the ion at m/z 305.3 following CID (Figure 1d). The product ion at m/z 140.1 corresponds to formation of an unsaturated piperidinium cation following elimination of the ester linkage at the 4-position of the piperidine.^[24] The presence of this ion provides evidence that the compound contains at least one tetramethylpiperidine group consisting of a secondary amine. The product ion at m/z 342.3 appearing above the precursor ion at m/z 305.3 confirming that the latter is a multiply charged species. The proposed structure of the ion is shown as an inset to Figure 1(d) and is consistent with the fragmentation mechanisms reported by Lowe *et al.* for ester-linked bifunctional HALS.^[23] These assignments are consistent with the proposed structure and its structural homology with TIN123 along with its apparent increase in

abundance upon weathering suggests that it is an *in situ* degradation product arising from TIN123.

Unlike the first degradation product discussed above, the presence of the ion at m/z 470.4 in Figures 1(a, b) cannot be directly attributable to *in situ* degradation of TIN123 as this ion is also observed when an authentic sample of TIN123 in solution is subjected to the same experimental conditions (data not shown). This suggests that the detection of this ion in Figures 1(a, b) may be due – at least in part – to in-source fragmentation of TIN123 consistent with the observation of this ion in the CID spectrum of m/z 737.6 previously reported.^[23] However, the increase in relative abundance of this ion with respect to ions corresponding to TIN123 (Figure 1b; m/z 369.4, 737.6) suggests that accelerated weathering may also facilitate *in situ* elimination of the ester-linkages at the piperidine 4-position. Such *cis*-elimination reactions are known to proceed at low temperatures^[25] and we have also proposed a free radical mechanism in a previous study of the 4-position chemistry in analogous TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) based compounds.^[24] The structural assignment of this ion was confirmed by the characteristic fragmentation patterns arising from CID of the precursor ion at m/z 470.4 (Figure 1e). The resulting product ions from the LESA-MS/MS spectrum are consistent with those previously reported from analysis of authentic TIN123 in solution by electrospray ionisation mass spectrometry (ESI-MS).^[23]





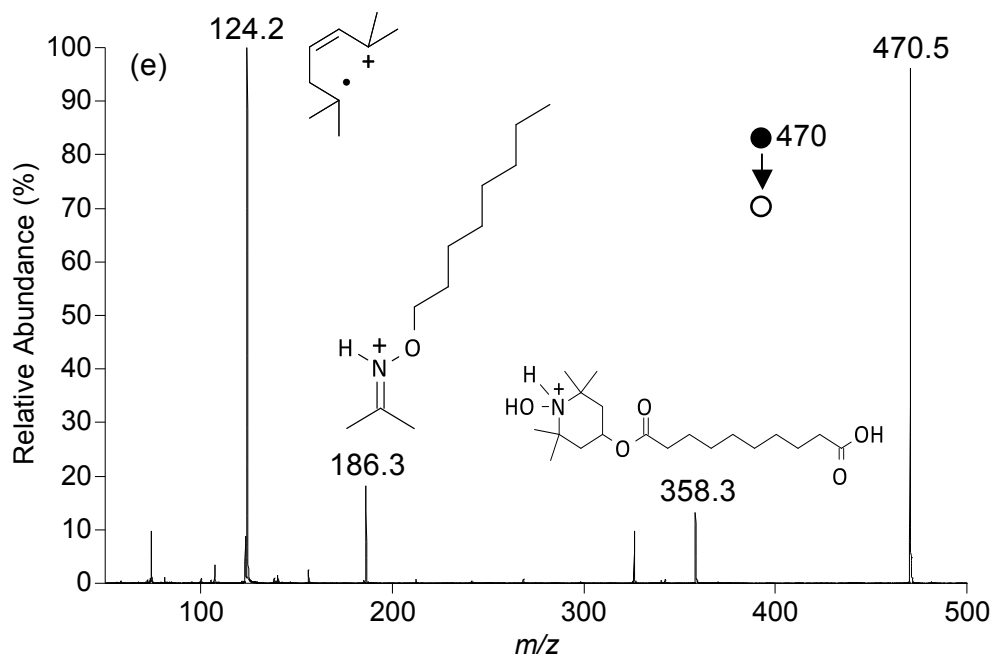


Figure 1. LESA-MS spectra acquired directly from cured polyester-based coil coatings containing TINUVIN 123; (a) with no exposure to UV light or heat and (b) after 900 hours within a Q-Sun xenon test chamber (Q-Lab Corporation, Westlake Ohio, USA). Positive ion LESA-MS/MS spectra following CID of ions at (c) m/z 369.4, (d) m/z 305.3 and (e) m/z 470.4 detected from a cured polyester-based coil coating.

Unstabilised Coil Coating

An unstabilised pigmented polyester-based coil coating (no HALS present) was exposed to outdoor field testing for four years at a site in Rockhampton, Australia and compared to a control sample (no outdoor exposure). The coil coatings were visually inspected to assess the aesthetic properties and the surface integrity of the coatings. True-colour images of both the control and a sample after four years of outdoor exposure are shown in

Figures 2(a) and (b), respectively. Figure 2(b) reveals the presence of powder-like deposits on the surface characteristic of polymer blooming, features that are absent on the control sample (Figure 2a). The result is a less aesthetically appealing coating with lower gloss and colour retention levels compared to the control. The source of the blooming is unknown but may be associated with degradation products accumulating at the surface on account of the weathering experienced by the polymer. In order to correlate blooming with any changes in chemistry at the surface of the coatings, analysis by LESA-MS was carried out on both the control and the weathered samples.

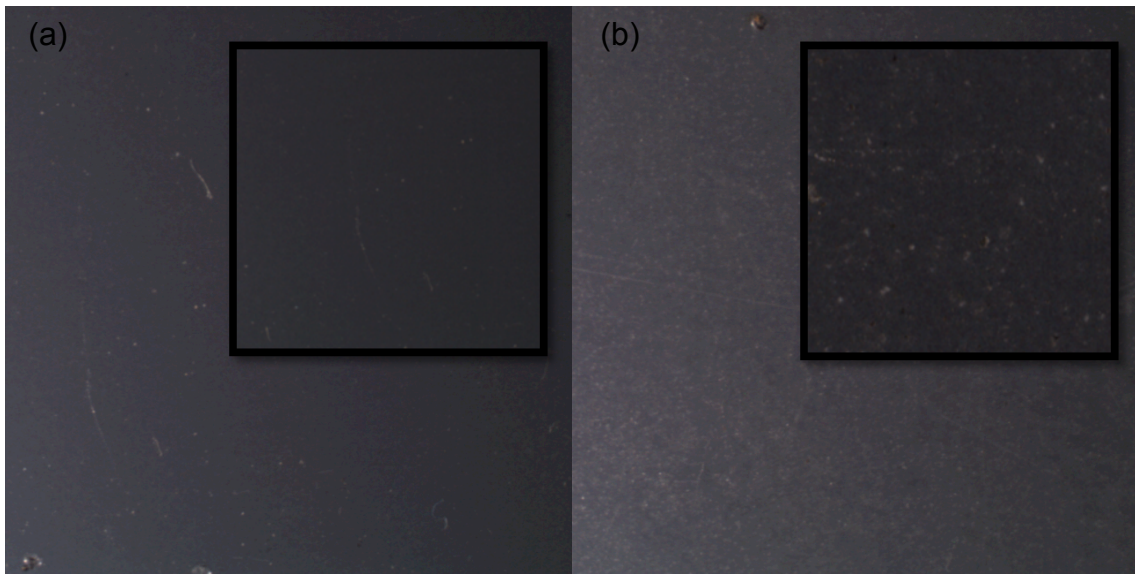
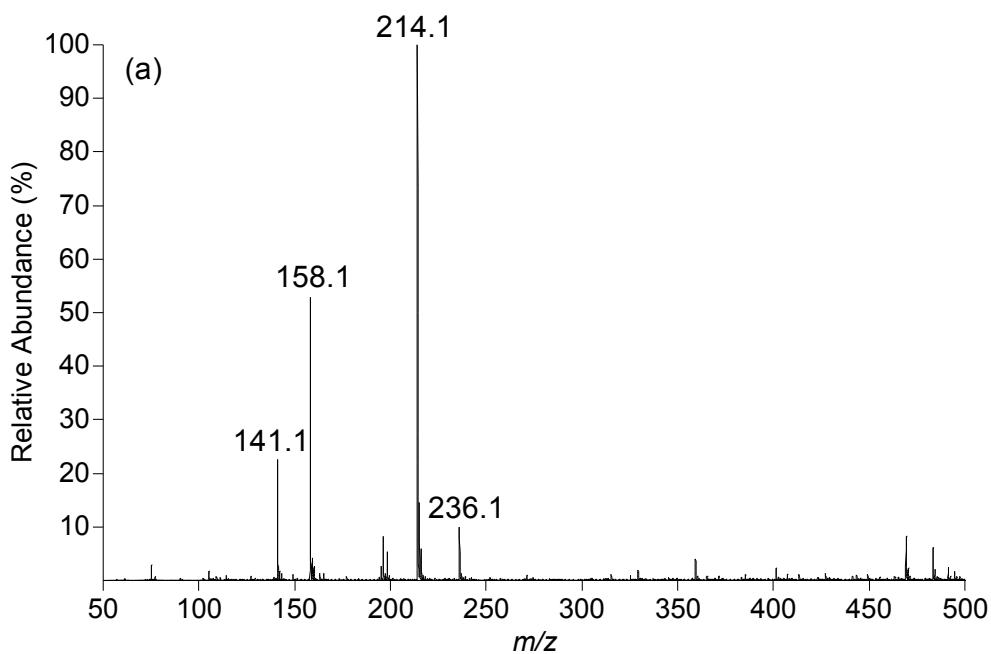


Figure 2. True-colour images of pigmented polyester-based coil coatings formulated without HALS: (a) control sample (no outdoor exposure) and (b) after four years exposure to outdoor field testing at a site in Rockhampton, Australia (Inset: 20x magnification).

The positive ion LESA-MS spectrum acquired from the control sample of the unstabilised coil coating yielded signals corresponding to common chemical noise of unknown origin (m/z 141.1 and 158.1) and a solvent contaminant *n*-butyl benzenesulfonamide (plasticiser) at m/z 214.1 and 236.1 corresponding to the $[M+H]^+$ and $[M+Na]^+$ ions respectively (Figure 3a). Analysis of the same polymer-based coating formulation after four years of outdoor field testing that included high temperatures and UV light exposure, an abundant ion at m/z 127 was detected (Figure 3b). The absolute signal intensities for the plasticiser $[M+Na]^+$ ion at m/z 236.1 is the same in Figures. 3(a) and (b), however, the absolute signal for the plasticiser $[M+H]^+$ ion at m/z 214.1 is lower in Figure 3(b) than it is Figure. 3(a). This suggests that the ion at m/z 127.1 is competing for charge with the plasticiser $[M+H]^+$ ion and other protonated species in solution indicating that the ion at m/z 127.1 is itself protonated. With the knowledge that this particular coil coating utilised melamine formaldehyde as a reactable crosslinker and given the possibility that the peak at m/z 127.1 may be the result of a singly charged protonated species, the chemical identity was tentatively assigned as protonated melamine (Figure 3c – inset). To confirm the structural identity of the ion detected at m/z 127.1, CID was performed with the resulting MS/MS spectrum shown in Figure 3(c). Fragmentation of precursor ions at m/z 127.1 generated abundant product ions at m/z 68.0 and 85.1 with minor products at m/z 60.0 and 110.1. These ions are consistent with those previously reported for the MS/MS of authentic protonated melamine under similar mass spectrometric conditions.^[26] Putative ion structures have been assigned to these fragmentation products based on the proposed fragmentation mechanism shown in Scheme 1. Following Scheme 1, assignment of the peaks in Figure 2 (c) correspond to the

losses of NH_3 (m/z 110.1) and NH_2CN (m/z 85.1) from protonated melamine. An ion at m/z 60.1 is also observed, arising from a competitive fragmentation process involving ring-opening of protonated melamine. The peak at m/z 68 corresponds to the loss of NH_3 from the ion at m/z 85 and is a result of the relatively high collision energy applied in this experiment, a phenomenon also observed by Yang and co-workers in the detection of authentic melamine and melamine in milk products.^[26]



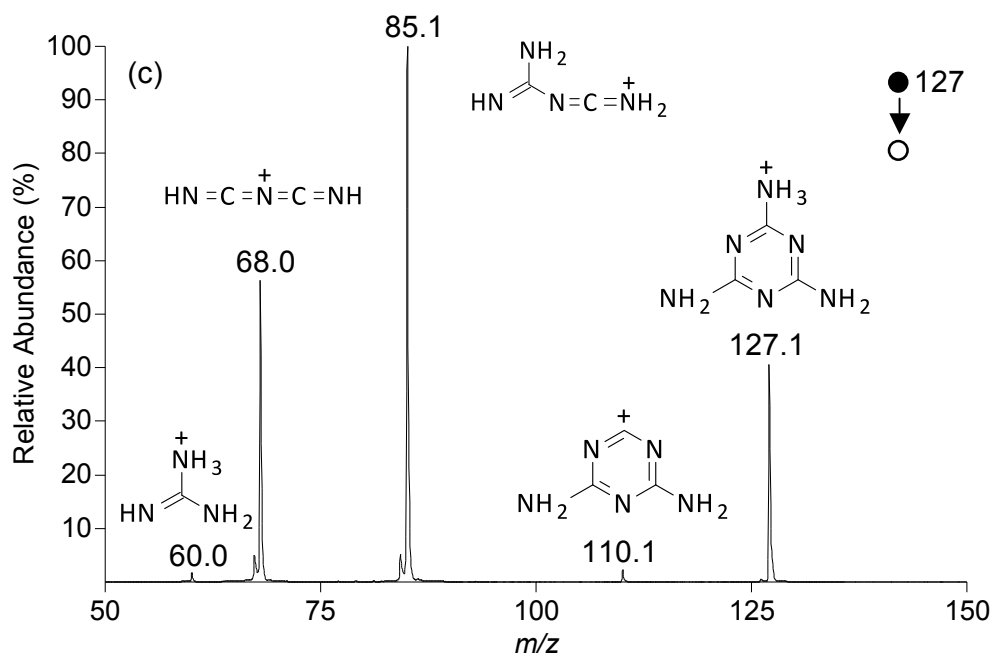
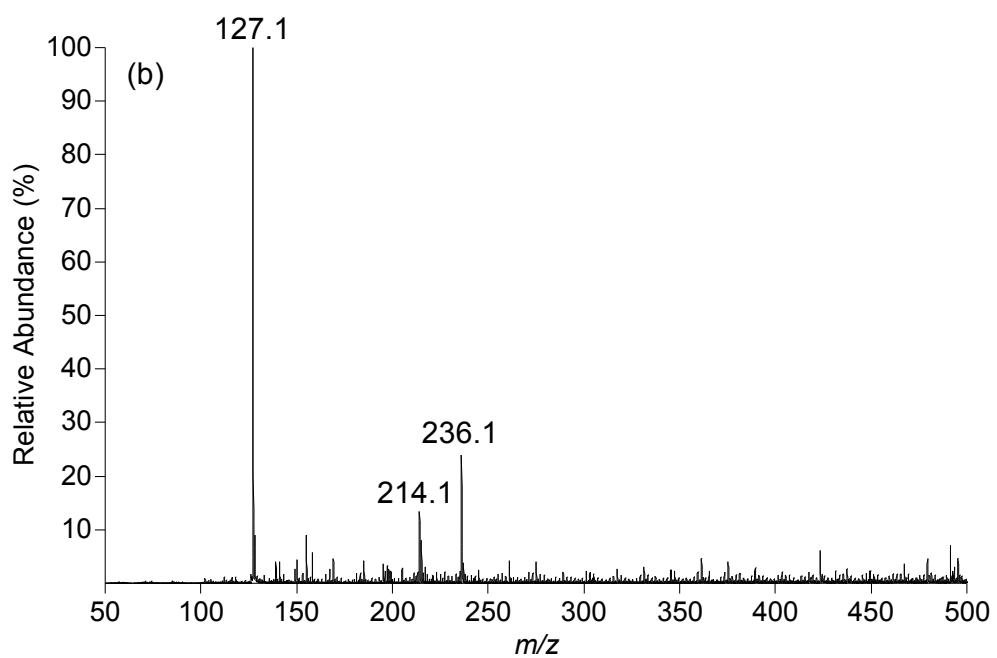
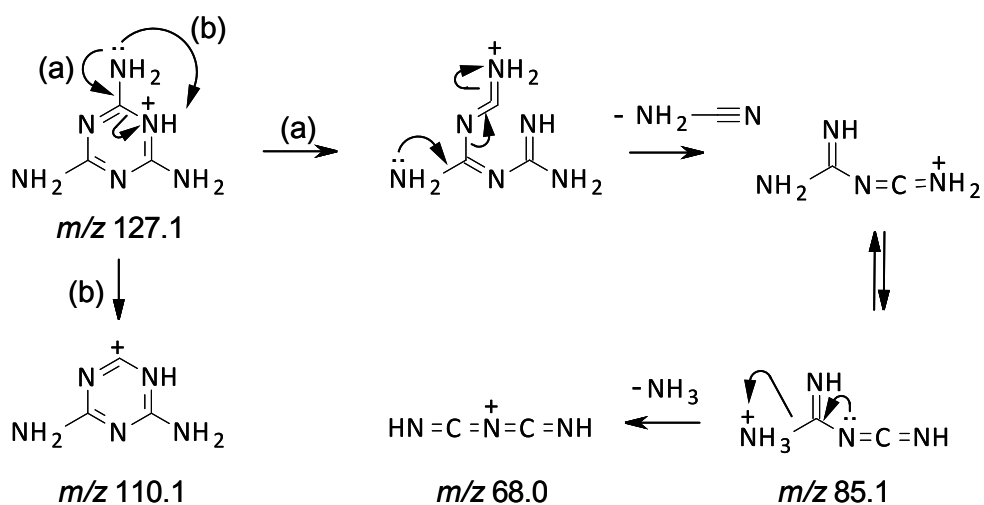


Figure 3. Positive ion LESA-MS spectra of pigmented polyester-based coil coatings formulated without HALS; (a) with no outdoor exposure (control sample) and (b) after four years exposure to natural weathering conditions at Rockhampton, Australia. (c) A LESA-MS/MS spectrum following CID of the ion at m/z 127 detected on the coatings surface after exposure to accelerated weathering; providing structural confirmation of the presence of melamine.



Scheme 1. The proposed fragmentation mechanism for protonated melamine (m/z 127) in the gas phase resulting from collision-induced dissociation.

Discussion and Conclusions

Liquid extraction surface analysis-mass spectrometry by means of a TriVersa NanoMate[®] ionisation source coupled to a QTRAP[®] 5500 triple quadrupole mass spectrometer has proven to be a fast, simple and effective method in the detection of a hindered amine light stabiliser from a polymer-based surface coating. Like other ambient MS techniques, LESA-MS analysis is able to be performed with the sample remaining under standard atmospheric conditions, however, LESA-MS is unique in that no sample preparation or pre-treatment is required other than cutting the sample to a workable size. In contrast, AP-MALDI-MS analysis requires the careful deposition of a matrix over the sample to facilitate desorption/ionisation. Photodissociation during MALDI of the HALS themselves (data not shown) can also lead to increased source fragmentation, complicating spectral analysis. Conversely, DESI-MS does not require the assistance of a matrix but instead uses a continuous flow of nebulised solvent directed at the sample surface to liberate and ionise the analyte. Unfortunately, the DESI-MS solvent flow is so minimal that suitable extraction of analyte from polymer-based surface coatings cannot be achieved thus requiring either (i) high temperatures (400 °C) that destroy the sample,^[27] or (ii) “swelling” the polymer in an atmosphere of solvent vapour prior to analysis in order to extract enough analyte to attain suitable detection levels.^[9] LESA-MS stands itself apart from these well established ambient MS methods as it separates the desorption (*i.e.*, extraction) and ionisation steps resulting in a much cleaner spectrum. For polymeric samples such as coil coatings, the desorption process combines localised swelling and extraction in a single automated step. By varying the solvent composition, the desorption process can be tailored to preferentially extract one analyte over another or

to control the depth of sampling from the polymer matrix by controlling the amount of swelling. For example, increasing the organic solvent content in the analysis of coil coatings would increase the effective sampling depth as a result of increased swelling. On the other hand, switching to a more aqueous solvent mixture would reduce swelling of the polymer and limit detection to analytes present on the surface of the coating only. The use of this technique has allowed detection of the hindered amine light stabiliser TIN123 from polymer samples and analysis of samples subjected to accelerated weathering has revealed two degradation products arising from TIN123. The first degradation product (Figure 1a, b; m/z 305) results from conversion of one *N*-ether piperidine moiety (*N*-OC₈H₁₇) within TIN123 to a secondary piperidine (*N*-H) to form (1-octyloxy-bis-(2,2,6,6-tetramethyl-4-piperidyl) sebacate. This product has been observed in a previous study with experimental evidence to suggest the degradation occurs via direct N-O bond homolysis.^[9] The second degradation product (Figure 1a, b; m/z 470) has not been reported previously but is consistent with predictions made by Marshall *et al.* that ester-linkages at the 4-position of 2,2,6,6-tetramethylpiperidine groups are susceptible to cleavage.^[24]

The ability to perform tandem mass spectrometric analyses also makes the technique powerful enough to identify changes in chemistry that may be associated with the degradation of the polymer itself. For instance, the detection of elevated levels of free melamine in a coil coating sample that has experienced four years of outdoor weathering compared to a sample left unexposed. The detection of melamine also correlates with changes in the coatings visual appearance with features indicative of polymer blooming present on the weathered sample. It is unclear if these physical changes are directly

attributable to the presence of melamine as a degradation product concentrating at the surface but may be indirectly responsible in association with one or more other materials, possibly an organic acid, capable of forming a hydrogen donor-acceptor complex.

These results represent the first reported case of LESA-MS analysis of polymers, demonstrating the potential for this technique to be an effective tool for high-throughput monitoring of polymer additive composition and polymer degradation products and may provide further insight into the mechanisms by which degradation occurs.

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References

- [1] D. Santos, M. R. Costa, M. T. Santos. Performance of polyester and modified polyester coil coatings exposed in different environments with high UV radiation. *Prog. Org. Coat.* **2007**, *58*, 296.
- [2] E. C. C. Association. Aware, 2009, *Introduction to Prepainted Metal*. last accessed: 28th June 2011. <http://www.prepaintedmetal.eu>.
- [3] M. P. Luda, G. Camino, E. Laurenti, S. Novelli, T. Temtchenko, S. Turri. Mechanism of photostabilization of perfluoropolyether coatings by hindered amine stabilisers. *Polym. Degrad. Stab.* **2001**, *73*, 387.
- [4] R. Spatafore, L. T. Pearson. Migration and blooming of stabilizing antioxidants in polypropylene. *Polym. Eng. Sci.* **1991**, *31*, 1610.
- [5] J. Pospisil, S. Nespurek. Photostabilization of coatings. Mechanisms and performance. *Prog. Polym. Sci.* **2000**, *25*, 1261.
- [6] D. Satas, A. A. Tracton. *Coatings Technology Handbook* 2nd ed. Marcel Dekker Inc., New York, **2001**.
- [7] J. F. Rabek. *Photostabilization of Polymers: Principles and Applications*. Elsevier Applied Science, London, UK, **1990**.
- [8] E. T. Denisov. The role and reactions of nitroxyl radicals in hindered piperidine light stabilisation. *Polym. Degrad. Stab.* **1991**, *34*, 325.
- [9] M. R. L. Paine, P. J. Barker, S. J. Blanksby. Desorption electrospray ionisation mass spectrometry reveals in situ modification of a hindered amine light stabiliser resulting from direct N-OR bond cleavage. *Analyst.* **2011**, *136*, 904.
- [10] J. L. Hodgson, M. L. Coote. Clarifying the mechanism of the Denisov cycle: how do hindered amine light stabilizers protect polymer coatings from photo-oxidative degradation? *Macromolecules.* **2010**, *43*, 4573.
- [11] F. Gugumus. The performance of light stabilizers in accelerated and natural weathering. *Polym. Degrad. Stab.* **1995**, *50*, 101.
- [12] C. M. Seubert, M. E. Nichols, A. V. Kucherov. Long-term weathering behavior of UV-curable clearcoats: depth profiling of photooxidation, UVA, and HALS distributions. *JCT Res.* **2005**, *2*, 529(10).
- [13] M. Kaci, N. Touati, R. Setnescu, T. Setnescu, S. Jipa. Characterization by chemiluminescence of unstabilized and HALS-stabilized LDPE films exposed to natural weathering conditions. *Int. J. Polym. Anal. Charact.* **2004**, *9*, 275.
- [14] J. L. Gerlock, A. V. Kucherov, M. E. Nichols. On the combined use of UVA, HALS, photooxidation, and fracture energy measurements to anticipate the long-term weathering performance of clearcoat/basecoat automotive paint systems. *J. Coat. Technol. Res.* **2001**, *73*, 45.
- [15] J. L. Gerlock, A. V. Kucherov, C. A. Smith. Determination of active HALS in automotive paint systems II: HALS distribution in weathered clearcoat/basecoat paint systems. *Polym. Degrad. Stab.* **2001**, *73*, 201.
- [16] Y. Taguchi, Y. Ishida, H. Matsubara, H. Ohtani. Quantitative analysis of an oligomeric hindered amine light stabilizer in polypropylene by matrix-assisted laser desorption/ionization mass spectrometry using a solid sampling technique. *Rapid Commun. Mass Spectrom.* **2006**, *20*, 1345.

- [17] Y. Taguchi, Y. Ishida, H. Ohtani, H. Bekku, M. Sera. Determination of a polymeric hindered amine light stabilizer in polypropylene formulated with magnesium hydroxide flame retardant by reactive thermal desorption-gas chromatography. *Anal. Sci.* **2004**, *20*, 495.
- [18] Y. Taguchi, Y. Ishida, H. Ohtani, H. Matsubara. Direct analysis of an oligomeric hindered amine light stabilizer in polypropylene materials by MALDI-MS using a solid sampling technique to study its photostabilizing action. *Anal. Chem.* **2004**, *76*, 697.
- [19] V. Kertesz, G. J. Van Berkel. Fully automated liquid extraction-based surface sampling and ionization using a chip-based robotic nanoelectrospray platform. *J. Mass Spectrom.* **2010**, *45*, 252.
- [20] G. A. Harris, A. S. Galhena, F. M. Fernandez. Ambient sampling/ionization mass spectrometry: applications and current trends. *Anal. Chem.* **2011**, *83*, 4508.
- [21] P. Marshall, V. Toteu-Djomte, P. Bareille, H. Perry, G. Brown, M. Baumert, K. Biggadike. Correlation of skin blanching and percutaneous absorption for glucocorticoid receptor agonists by matrix-assisted laser desorption ionization mass spectrometry imaging and liquid extraction surface analysis with nanoelectrospray ionization mass Spectrometry. *Anal. Chem.* **2010**, *82*, 7787.
- [22] D. Eikel, J. Henion. Liquid extraction surface analysis (LESA) of food surfaces employing chip-based nano-electrospray mass spectrometry. *Rapid Commun. Mass Spectrom.* **2011**, *25*, 2345.
- [23] T. A. Lowe, M. R. L. Paine, D. L. Marshall, L. A. Hick, J. A. Boge, P. J. Barker, S. J. Blanksby. Structural identification of hindered amine light stabilisers in coil coatings using electrospray ionisation tandem mass spectrometry. *J. Mass Spectrom.* **2010**, *45*, 486.
- [24] D. L. Marshall, M. L. Christian, G. Gryn'ova, M. L. Coote, P. J. Barker, S. J. Blanksby. Oxidation of 4-substituted TEMPO derivatives reveals modifications at the 1- and 4-positions. *Org. Biomol. Chem.* **2011**, *9*, 4936.
- [25] G. Gryn'ova, J. L. Hodgson, M. L. Coote. Revising the mechanism of polymer autooxidation. *Org. Biomol. Chem.* **2011**, *9*, 480.
- [26] S. Yang, J. Ding, J. Zheng, B. Hu, J. Li, H. Chen, Z. Zhou, X. Qiao. Detection of melamine in milk products by surface desorption atmospheric pressure chemical ionization mass spectrometry. *Anal. Chem.* **2009**, *81*, 2426.
- [27] S. Reiter, W. Buchberger, C. Klampfl. Rapid identification and semi-quantitative determination of polymer additives by desorption electrospray ionization/time-of-flight mass spectrometry. *Anal. Bioanal. Chem.* **2010**, *400*, 2317.