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Temperature-programmed packed capillary liquid chromatography coupled to evaporative light-scattering detection and electrospray ionization time-of-flight mass spectrometry for characterization of high-molecular-mass hindered amine light stabilizers

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Abstract

High-molecular weight-hindered amine light stabilizers (HMW-HALSs) are of utmost importance in modern polyolefin stabilization technology and in-depth knowledge about their chemical composition, particularly the oligomers, is essential for development of new and more efficient stabilizers. In the present study, the applicability of temperature-programmed packed capillary LC coupled to miniaturized ELSD and positive mode ESI–TOF–MS for analysis of HMW-HALSs is demonstrated through extensive characterization of two state-of-the-art stabilizers, i.e., HALS-1 and HALS-2. Both stabilizers were individually separated on a 320 μm i.d. × 35 cm long Hypersil 3 μm ODS-100 column using a temperature program from 30 to 120 °C and a quaternary mixture of ethylacetate, acetonitrile, triethylamine (TEA) and acetic acid (45.0:44.9:10.0:0.1 (v/v/v/v)) as the mobile phase. The effect of using various amounts of ethylacetate, acetonitrile and triethylamine in the mobile phase on the chromatographic separation is demonstrated. Furthermore, the LC–ESI–TOF–MS analyses revealed that HALS-1 (oligomeric) was highly complex and consisted of at least five different mass series, while HALS-2, which was assumed to be monomeric, contained two different mass series. Chemical structures for nearly all species of both stabilizers are proposed.
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Keywords: Temperature programming; Evaporative light-scattering detection; Hindered amine light stabilizers

1. Introduction

Exposure to light and oxygen induce reactions in polyolefins that can cause discoloration and impairment of the mechanical properties, e.g., cracking and loss of tensile or impact strength [1–3]. Hence, the lifetime of unprotected polyolefin products usually is short when exposed to such conditions. Over the past four decades, however, advances in polyolefin stabilization using polymer additives have pushed the performance boundaries of polyolefin products to unpredicted levels. These achievements are mainly based on breakthroughs in hindered amine chemistry, which consequently have led to the development of so-called hindered amine light stabilizers (HALSs). These compounds are mainly derivatives of 2,2,6,6-tetramethylpiperidine with high protecting efficiency in polyolefins even at concentrations less than 1% (w/w). Since the introduction of the first commercial HALS in 1973, namely the bis(2,2,6,6-tetramethylene-4-piperidinyl)sebacate [4], a wide range of low and high-molecular weight (HMW)-HALSs have been developed. Fig. 1 shows the chemical structures of an oligomeric and a monomeric HMW-HALS, from here called HALS-1 and HALS-2. Both have high compatibility in polyolefins, low volatility and high extraction resistance because of their high MW, which make them especially useful in thin products such as fibers and films. The main advantage of HALS-2 is that it enhances the color yield of pigmented polyolefin products, while HALS-1 provides minimal pigment interaction and improved melt flow control. Moreover, both HALSs are also effective as antioxidants and contribute significantly to the long-term heat stability of polyolefins.

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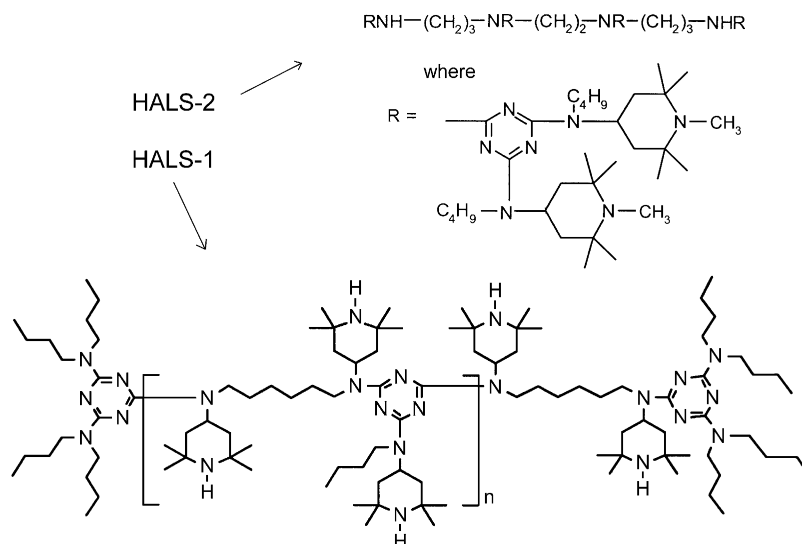

Fig. 1. The chemical structures of HALS-1 and HALS-2.

HMW-HALSs are not easily analyzed with traditional gas chromatography (GC) or supercritical fluid chromatography (SFC), because of low volatility and numerous basic amino groups. Liquid chromatography (LC), on the other hand, has been used for "single peak"-elution and determination of HALSs in polyolefins by the plastic industries for more than two decades [5–14]. HALSs are commonly used in combinations with other additives, e.g., antioxidants, and LC separations are therefore often necessary in order to obtain reliable quantification. However, separation of individual HALS species is also of great interest since there are many potential applications requiring exact knowledge of the molecular heterogeneity, e.g., development of new tailor-made HALSs for use in polyolefin products with specific performance attributes [15]. Moreover, sufficient separation also facilitates the calculation of classical polymer parameters such as the weight-average molecular mass [16]. The coupling of a high-resolution LC technique with detectors that can provide both structural and quantitative information would therefore give new and valuable insight to the chemical composition of these complex compounds.

The authors have previously demonstrated that temperature-programmed non-aqueous reversed-phase packed capillary LC–ELSD can provide excellent resolution of complex mixtures of HALS oligomers, i.e., Tinuvin 622 [17] and Chimassorb 944 [18]. Packed capillary LC–ELSD is characterized by high resolution of complex mixtures when using long columns, large savings in organic solvent consumption, and even more important; the miniaturized ELSDs are particularly useful for characterization of polymeric compounds due to more or less universal and linear response [19–22]. However, the response of the ELSD is reported to increase with decreased polarity of the mobile phase [23,24], and unfortunately it can change during solvent gradient applications. For such applications, the replacement of the solvent gradient with a temperature program, if possible, is often an attractive alternative. In contrast to conventional sized LC columns, packed capillary LC columns are well suited for operation at various temperatures because of their low thermal mass [25]. Thus, narrow LC columns create new opportunities for retention control and selectivity tuning with the application of temperature programming [25–39]. In the present paper, temperature-programmed packed capillary LC coupled to ELSD and ESI–TOF–MS has been used for characterization of the two latest members of an important group of additives within polyolefin stabilization technology, i.e., the HALSs. Firstly, the previously developed LC–ELSD method [18] was adapted and optimized for the separation of HALS-1 and HALS-2. Secondly, the peaks in the ELSD chromatograms were identified by coupling the LC system to positive mode ESI–TOF–MS.

2. Experimental

2.1. Chemicals and materials

Ethylacetate (Labscan, Dublin, Ireland) and acetonitrile (Rathburn Chemicals, Walkerburn, Scotland) were both of HPLC grade quality, while triethylamine (TEA) (Sigma–Aldrich Chemie, Steinheim, Germany) were of P.A. quality. Totally porous spherical 3 μm Hypersil ODS particles with an average pore diameter of 100 Å were obtained from Thermo Hypersil-Keystone (Runcorn, Cheshire, UK), while nitrogen (99.6%) and helium (99.998%) were purchased from AGA (Oslo, Norway).

2.2. Preparation of mobile phases and columns

The mobile phases were filtered through 0.45 μm Minisart-RC25 filters from Sartorius (Göttingen, Germany) and degassed with 99.998% helium for 10 min daily. The

totally porous spherical 3 μm Hypersil ODS particles were packed into 0.32 mm i.d. (0.45 mm o.d.) × 35 cm long polyimide-coated fused silica capillaries from Polymicro Technologies (Phoenix, AZ, USA) using a downward high-pressure liquid slurry method that has been developed in-house.

2.3. Packed capillary LC–ELSD experiments

An Eldex Micro-Pro dual syringe pump (Eldex Laboratories, Napa, CA, USA) was used to deliver a constant flow rate of 5 μl min^{-1} throughout the study. Manual injections were performed with a Valco ChemInert model C4 injection valve (Valco Instruments, Houston, TX, USA) equipped with a 0.5 μl internal loop. A Varian 3400 CX GC oven (Varian, Palo Alto, CA, USA) was used to control the temperature of the capillary column, while detection was accomplished using a Varex Mark III ELSD from Alltech Associates (Deerfield, IL, USA) equipped with a modified nebulizer [21,22]. The drift tube temperature of the detector was set to 90 °C, while 99.6% nitrogen (2.20 l min^{-1}) was used as the nebulizing gas. The column inlet was connected to the injector with a 75 μm i.d. × 25 cm fused silica capillary, while the column outlet was connected directly to the nebulizer of the ELSD with a 20 μm i.d. × 40 cm fused silica capillary. This capillary also worked as a linear restrictor preventing the mobile from boiling at higher temperatures. TotalChrom 6.2 Workstation software (Perkin-Elmer Instruments, Wellesley, MA, USA) was used for data sampling.

2.4. Packed capillary LC–ESI–TOF–MS experiments

For LC–MS analysis, the chromatographic set-up described in Section 2.3 was detached from the ELSD and connected to a Micromass LCT TOF–MS (MicroMass, Manchester, UK). The TOF–MS instrument was equipped with a Z-spray atmospheric pressure ionization source for ESI, which was modified to handle flow rates in the low μl min^{-1} range. Ionization was performed in the positive mode, with capillary voltage set at +2.4 kV. The sample and extraction cone was operated at +15 V and +3 V, respectively. No nebulizer gas was required in order to obtain stable spray performance, while the drying gas flow rate was set to 200 l h^{-1}. The temperature on the ESI interface was 80 °C. The ESI–TOF–MS instrument was controlled and data were acquired using the Masslynx version 3.5 software from Micromass. The mass spectra were recorded in the m/z range of 500–10,000.

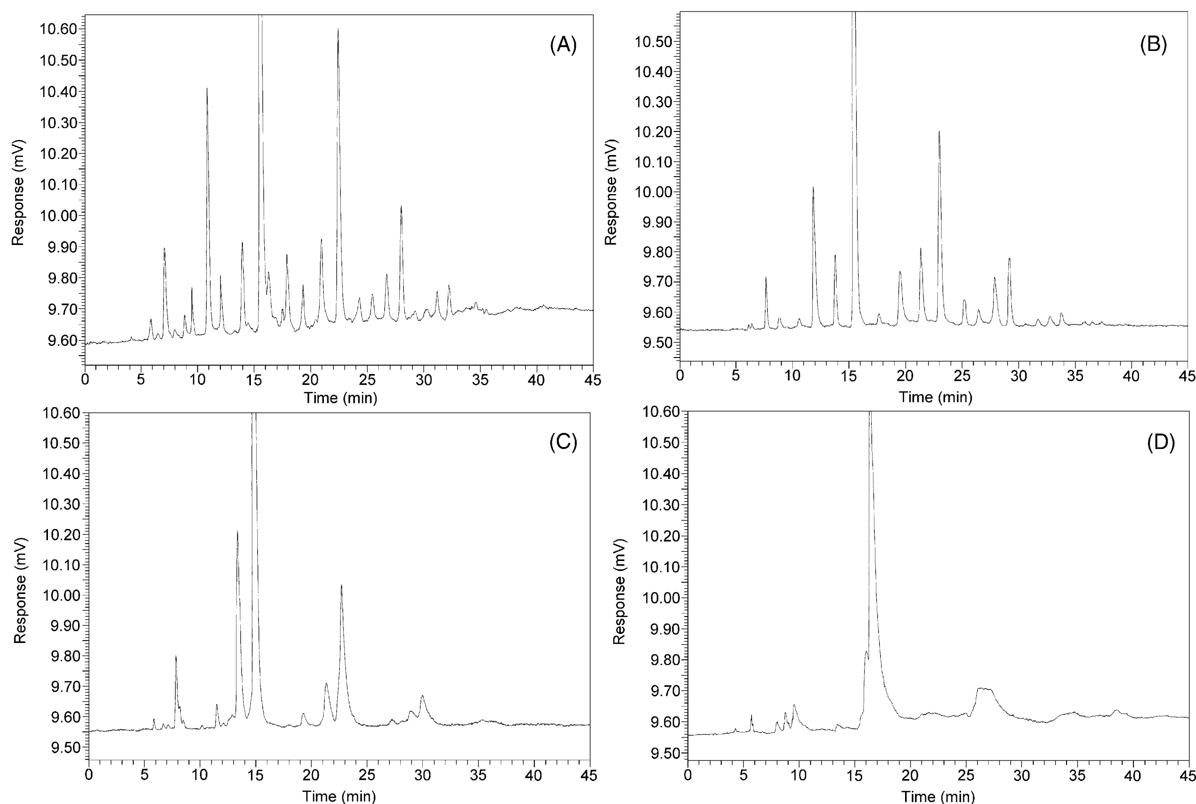

Fig. 2. Temperature-programmed packed capillary LC–ELSD separation of HALS-1 using different compositions of ethylacetate, ACN and TEA in the mobile phase. The percentage compositions of etylacetate, ACN and TEA (v/v/v) were: (A) 45.0:45.0:10.0, (B) 55.0:44.0:1.0, (C) 67.0:32.7:0.3 and (D) 70.0:29.9:0.1. Flow rate: 5 μl min^{-1}. Column: 3 μm Hypersil ODS-100, 0.32 mm i.d. × 35 cm. Temperature program: 30 °C for 2 min, then 2 °C min^{-1} to 120 °C.

3. Results and discussion

3.1. Chromatographic considerations

HMW-HALSs are large, lipophilic compounds with numerous secondary and/or tertiary basic amino groups that tend to adsorb strongly to different types of surfaces. Matuska et al. found that it was necessary to add triethylamine to the methanol utilized for precipitation of the toluene-dissolved (refluxed) polymer to prevent analyte adsorption to laboratory glassware and filter-papers during analysis of Chimassorb 944 in polyolefins [12]. The authors have previously found that addition of 10 vol.% TEA in the mobile phase was necessary to elute Chimassorb 944 with acceptable peak shapes from a capillary column packed with porous C18-modified silica-based particles [18]. Consequently, the initial separations of HALS-1 were performed with the same chromatographic conditions as in the previously developed method [18], except for two minor modifications. The ethylacetate content in the mobile phase was increased with 5 vol.%, and a temperature program starting at 30 °C for 2 min, then increasing 2 °C min^{-1} up to 120 °C was found to be the best compromise between resolution and analysis time (Fig. 2A). Under these conditions, HALS-1 was separated into almost 30 peaks in less than 40 min. Normally, high concentrations of amines in the mobile phase are not desirable when performing positive mode ESI–MS of basic analytes, since it may suppress the formation of gas-phase analyte ions [40,41]. Therefore, an effort was made to reduce the amount of TEA in the mobile phase, but as shown in Fig. 2A–D, the composition of ethylacetate, ACN and TEA had a strong influence

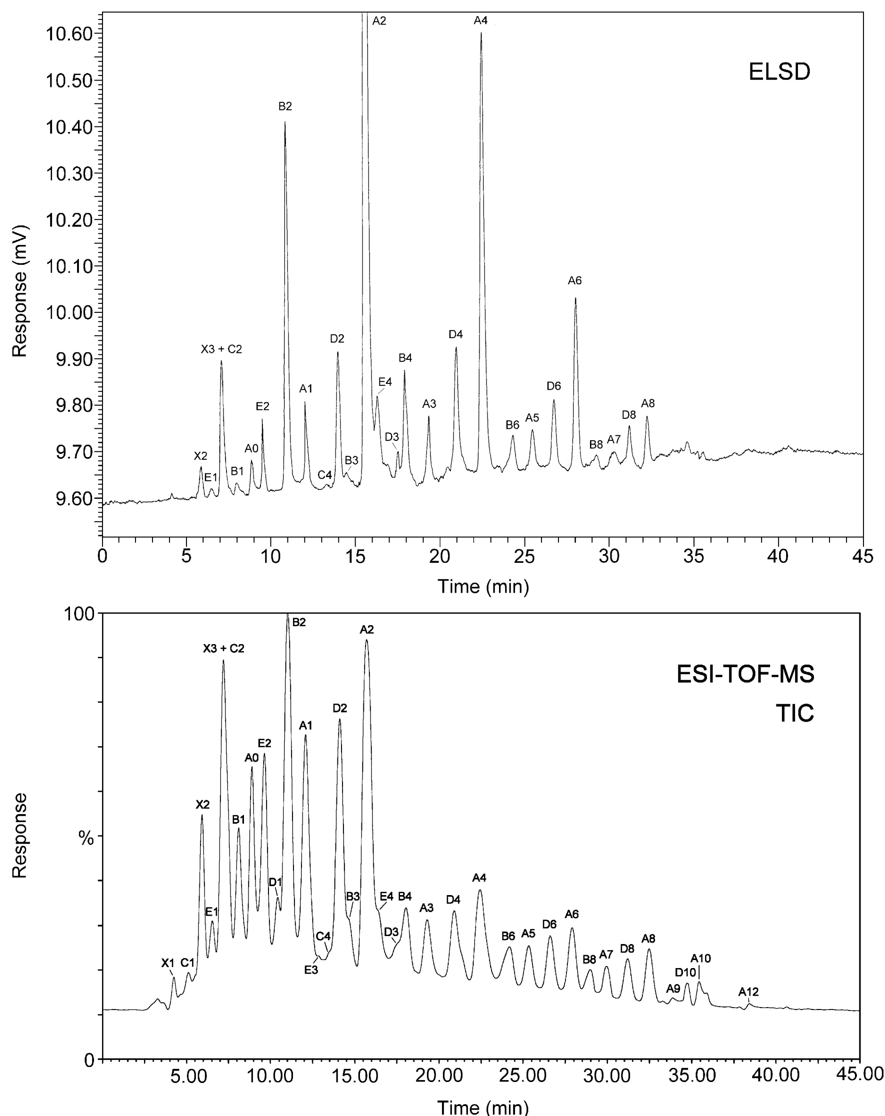

Fig. 3. Separation of HALS-1 using temperature-programmed packed capillary LC coupled to ELSD and ESI–TOF–MS. Mobile phase: ethylacetate–ACN–TEA–acetic acid (45:44.9:10:0.1 (v/v/v/v)). Flow rate: 5 µl min^{-1}. Column: 3 µm Hypersil ODS-100, 0.32 mm i.d. × 35 cm. Temperature program: 30 °C for 2 min, then 2 °C min^{-1} to 120 °C.

on the chromatographic behavior of the HALS-1 species. Note that the relative amounts of ethylacetate and ACN were adjusted so that the base peak eluted at approximately 15 min in all chromatograms, since the amount of TEA not only had a strong effect on the on the peak widths and peak shapes, but also on the retention factors. Although the addition of 1 vol.% TEA gave acceptable efficiency and peak shapes, the selectivity was different and the resolution was not equally good. Consequently, it was decided to try to use 10 vol.% of TEA in the mobile phase also in the LC–ESI–TOF–MS experiments.

3.2. Characterization of HALS-1

In principle, the m/z range of the TOF–MS is unlimited and the only restrictions arise in ion production and detection. Furthermore, the ability to register ion packages of all masses simultaneously provides high sensitivity over the full spectrum. These properties make the TOF–MS particularly suited for characterization of complex samples with m/z values higher than the range of most quadruples, e.g., the HMW-HALSs. In the preliminary ESI–TOF–MS investigations, a 10 $\mu g\,ml^{-1}$ solution of HALS-1 was introduced

Table 1
Experimental data from the LC–ELSD and LC–ESI–TOF separations of HALS-1 shown in Fig. 3

Peak no.[a]	m/z[b] $(MW + H)^+$	R_t LC–MS[c] (min)	R_t LC–ELSD[d] (min)	Peak area[e] (μV s)
A0	1062	8.92 ± 0.02	8.89 ± 0.03	1486 ± 49
A1	1744	12.10 ± 0.04	12.08 ± 0.05	3423 ± 64
A2	2425	15.70 ± 0.09	15.68 ± 0.08	44630 ± 549
A3	3107	19.38 ± 0.12	19.36 ± 0.10	2411 ± 61
A4	3788	22.59 ± 0.11	22.56 ± 0.11	17131 ± 250
A5	4470	25.52 ± 0.14	25.49 ± 0.15	2276 ± 59
A6	5152	28.10 ± 0.15	28.08 ± 0.16	6396 ± 116
A7	5833	30.32 ± 0.18	30.30 ± 0.18	1280 ± 35
A8	6515	32.30 ± 0.19	32.27 ± 0.17	1962 ± 51
A9	7196	33.84 ± 0.19	33.81 ± 0.19	[f]
A10	7878	35.39 ± 0.18	35.36 ± 0.19	[f]
A12	8560	38.43 ± 0.17	38.41 ± 0.18	[f]
B1	1410	8.11 ± 0.03	8.09 ± 0.02	1078 ± 39
B2	2092	11.00 ± 0.05	10.98 ± 0.04	12824 ± 204
B3	2774	14.42 ± 0.07	14.38 ± 0.07	1151 ± 35
B4	3455	18.00 ± 0.08	17.97 ± 0.09	4559 ± 84
B5	4137	21.43 ± 0.11	21.41 ± 0.12	[f]
B6	4818	24.39 ± 0.16	24.37 ± 0.15	1965 ± 50
B7	5500	27.00 ± 0.18	26.97 ± 0.16	[f]
B8	6182	29.28 ± 0.19	29.25 ± 0.19	924 ± 27
C1	1077	5.36 ± 0.01	5.33 ± 0.01	[f]
C2	1759	7.16 ± 0.01	7.14 ± 0.02	1267 ± 36
C3	2440	10.24 ± 0.05	10.26 ± 0.04	[f]
C4	3122	13.33 ± 0.07	13.35 ± 0.05	135 ± 16
D1	1604	10.56 ± 0.04	10.53 ± 0.04	[f]
D2	2286	14.04 ± 0.05	14.01 ± 0.06	4147 ± 66
D3	2968	17.54 ± 0.08	17.52 ± 0.09	1246 ± 36
D4	3649	21.03 ± 0.11	21.01 ± 0.11	6018 ± 90
D5	4331	23.94 ± 0.16	23.91 ± 0.14	[f]
D6	5012	26.80 ± 0.15	26.77 ± 0.15	3245 ± 66
D7	5694	29.11 ± 0.15	29.08 ± 0.16	[f]
D8	6376	31.22 ± 0.15	31.20 ± 0.16	2118 ± 49
D10	7738	34.74 ± 0.16	34.72 ± 0.16	[f]
E1	1271	6.52 ± 0.03	6.49 ± 0.01	383 ± 30
E2	1953	9.58 ± 0.03	9.54 ± 0.03	1481 ± 40
E3	2634	12.85 ± 0.05	12.82 ± 0.06	[f]
E4	3316	16.36 ± 0.09	16.34 ± 0.10	2205 ± 54
X1	1226	5.92 ± 0.02	5.90 ± 0.01	1153 ± 38
X2	1365	7.18 ± 0.02	7.16 ± 0.01	3824 ± 74

[a] From Fig. 3.
[b] Observed monoisotopic m/z values with LC–ESI–TOF–MS. Suggested chemical structures are shown in Fig. 4.
[c] Average retention times obtained with LC–ESI–TOF–MS ($n = 3$).
[d] Average retention times obtained with LC–ELSD ($n = 3$).
[e] Average peak areas obtained with LC–ELSD ($n = 3$).
[f] detected with LC–ESI–TOF–MS (low abundance), but not with LC–ELSD.

into the ion source by direct infusion. When HALS-1 was dissolved in the mobile phase (see Fig. 2A), only low abundant analyte ions with $m/z < 5,000$ were observed. However, when 0.1 vol.% of acetic acid was added to the solution, an abundance of singly protonated ions with m/z values up to almost 9000 were detected. Furthermore, only a two-fold increase in S/N ratio was observed when the concentration of acetic acid was raised from 0.1 to 1 vol.%. The former concentration was therefore applied in the mobile phase, since it was found to have a negligible effect on the retention factors of the already developed HALS-1 separation.

Fig. 3 shows the temperature-programmed packed capillary LC–ELSD and LC–ESI–TOF–MS chromatograms of HALS-1. Although the response of the two detectors was different, the retention times of the different HALS-1 species were highly identical, as shown in Table 1. The overall slightly longer retention times obtained with the LC–ESI–TOF–MS separation was probably due to the additional dead volume of the electrospray needle. The ESI–TOF–MS investigations revealed that the chemical composition of HALS-1 was very complex, and Table 1 shows the m/z values of the singly protonated isotopic masses that were observed when extracting mass spectra from the peaks obtained in the TIC chromatogram. By comparing the observed masses with the structural formula of HALS-1, it was realized that there were at least five different mass series present in the product. In Fig. 4, structural formulas for the A-, B- and C-series are suggested. These suggestions also fit reversed-phase LC theory, since the retention times of the B-series are shorter than the A-series, while the retention times of the C-series are shorter than the B-series (Table 1). In addition, the difference in retention time between the three series was relatively equal. Regarding the last two series, i.e. the D- and E-series, it was calculated that the experimental difference in monoisotopic mass between not only the A- and D-series, but also between the B- and E-series, was close to 139 mass units. This corresponds to substitution of one of the 2,2,6,6-tetramethylpiperidinyl groups (monoisotopic MW = 140.1 g mol^{-1}) with one hydrogen-atom. Again, this is supported by the elution order, since the D- and E-series have slightly shorter retention times than the A- and B-series, respectively.

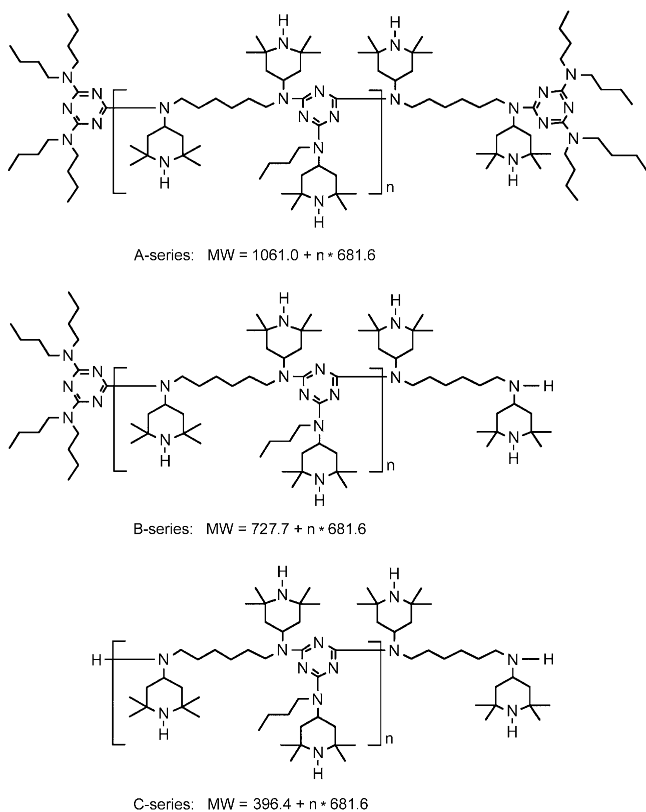

Fig. 4. Suggested chemical structures for the A-, B-, and C-series of HALS-1 with the corresponding monoisotopic molecular weights.

3.3. Characterization of HALS-2

Although HALS-2 is a monomer, it is defined as a HMW stabilizer due to its impressive size (monoistopic MW =

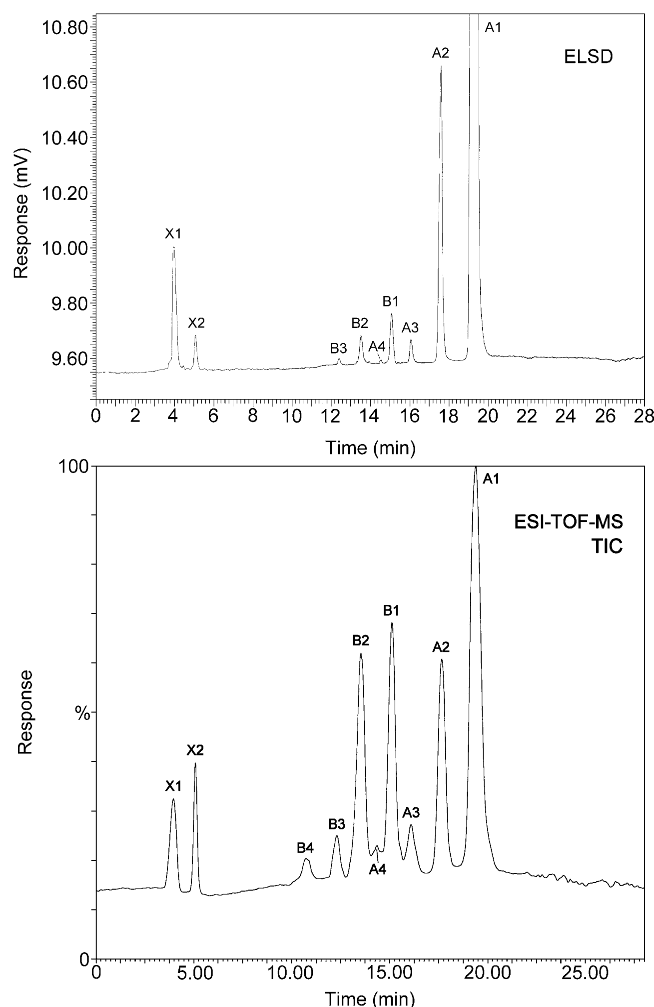

Fig. 5. Separation of HALS-2 using temperature-programmed packed capillary LC coupled to ELSD and ESI–TOF–MS. Same conditions as described in Fig. 3.

Table 2
Experimental data from the LC–ELSD and LC–ESI–TOF–MS separations of HALS-2 shown in Fig. 5

Peak no.[a]	m/z[b] $(MW + H)^+$	R_t LC–MS[c] (min)	R_t ELSD[d] (min)	Peak area[e] (μV s)
A1	2285	19.37 ± 0.13	19.31 ± 0.12	101129 ± 1412
A2	2271	17.67 ± 0.12	17.64 ± 0.11	14224 ± 254
A3	2257	16.09 ± 0.08	16.07 ± 0.09	1660 ± 66
A4	2243	14.59 ± 0.07	14.56 ± 0.07	160 ± 16
B1	1772	15.14 ± 0.06	15.11 ± 0.08	2706 ± 88
B2	1758	13.55 ± 0.06	13.53 ± 0.06	1849 ± 67
B3	1744	12.47 ± 0.06	12.43 ± 0.06	311 ± 27
B4	1730	10.77 ± 0.05	[f]	–
X1	$n \times 283$	5.13 ± 0.02	5.09 ± 0.02	5458 ± 136
X2	546	4.02 ± 0.02	3.98 ± 0.01	1837 ± 66

[a] From Fig. 5.
[b] Observed monoisotopic m/z values with LC–ESI–TOF–MS. Suggested chemical structures are shown in Fig. 6.
[c] Average retention times obtained with LC–ESI–TOF–MS ($n = 3$).
[d] Average retention times obtained with LC–ELSD ($n = 3$).
[e] Average peak areas obtained with LC–ELSD ($n = 3$).
[f] detected with LC–ESI–TOF–MS, but not with LC–ELSD.

$2284\,g\,mol^{-1}$). As already shown in Fig. 1, it is made by the attachment of four R-groups to the base molecule. When HALS-2 was separated under exactly the same conditions as HALS-1, it split into two different series, which is shown in Fig. 5. At first sight, the different retention and similar distribution of the two series indicate that the A-series has four R-groups, while the B-series has only three. The ESI–TOF–MS analysis confirmed that HALS-2 contained two different mass series, but surprisingly it was the difference in mass units between A1 and B2, A2 and B3, A3 and B4, etc., that corresponded to the mass of one R-group (Table 2). The monoisotopic mass of one R-group was calculated to $528\,g\,mol^{-1}$. However, Table 2 also shows that the difference in mass units between the species of both series was only 14. A possible explanation is that HALS-2 has been methylated to cover any non-reacted sites on the base molecule, which also can methylate the N-atoms in the 2,2,6,6-tetramethylpiperidinyl groups. Since derivatization of compounds with several possible reaction sites often gives by-products, different degrees of methylation can explain the $n \times 14$ difference in mass units observed within both series. The suggested chemical structures for the A- and B-series are illustrated in Fig. 6. Nevertheless, if this was the case, the methylene selectivity of the ODS column was remarkable, since the mass of one methyl group is less than 1% of the mass of the separated molecules. Regarding the peaks labeled X1 and X2 in Fig. 5, structural suggestions are not easily presented. However, as described in Table 2, X1 is most likely a polymeric compound with a mass distribution of $n \times 283$, while X2 probably is excessive amounts of R-groups, e.g., present as R–OH.

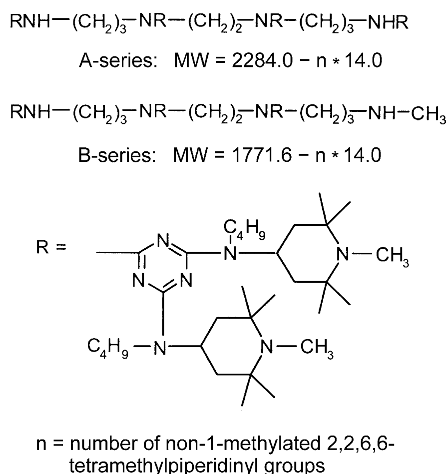

Fig. 6. Suggested chemical structures for the A- and B-series of HALS-2 with the corresponding monoisotopic molecular weights. Note that the placement of the three R-groups of the B-series is arbitrary.

4. Conclusions

The strengths of the applied capillary LC–ELSD/ESI–TOF–MS methodology are all attributed to the low flow rate of the capillary LC column: (1) the opportunity to apply temperature programming, (2) the splitless coupling to the ESI interface, and (3) a more than 200-fold savings of organic solvents compared to a 4.6 mm i.d. column. The temperature-programmed reversed-phase LC separation provided excellent resolution of never before resolved HMW-HALSs, and is thus a highly attractive alternative to more traditional separation techniques, e.g., gel-permeation chromatography (GPC). Although an unusually high mobile phase concentration of TEA was necessary to elute the different HALS-1 and HALS-2 species with acceptable column efficiencies and peak shapes from the C18 silica-based column, positive mode ESI produced an abundance of singly protonated molecular ions when only 0.1 vol.% of acetic acid was added to the mobile phase. Consequently, the developed HALS separations could be

coupled to ESI–TOF–MS for identification of the different HALS species. Altogether, the combined results of the LC–ELSD and the LC–ESI–TOF–MS analyses revealed that HALS-1 and HALS-2 were relatively impure products, which indicate that significant gains in performance are achievable by optimizing the synthesis procedures. The results also indicate that the present methodology has the potential of becoming the benchmark for characterization of HMW-HALSs.

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