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Short communication

# Hindered amine stabilizers investigated by the use of packed capillary temperature programmed liquid chromatography II: Poly-(*N*- $\beta$ -hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxypiperidyl succinate)<sup>☆</sup>

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## Abstract

Three different trademark products of a hindered amine stabilizer with the IUPAC name poly-(*N*- $\beta$ -hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxypiperidyl succinate), have been analyzed and compared to each other by the use of packed capillary temperature programmed liquid chromatography and light scattering detection. The analysis by this method has shown that the products contained approximately 50 different homologues and/or other components. The method also demonstrated its potential in purity control of products from different manufacturers. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Degradation (oxidation) of polyolefins like polypropylene (PP) and polyethylene (PE) is accelerated outdoors because of UV-radiation and the presence of oxygen. By introducing oligomeric hindered amine stabilizers (HAS) into the polyolefin, the polymer itself is protected against such degradation.

Oligomeric HAS compounds are especially known to be very effective antioxidants in thin materials as fibre and films, because of their low volatility and extractability [1]. The amount of HAS used in polyolefin products depends on where the product is supposed to be used, and also on the expected lifetime. However, relative high quantities of the HAS antioxidant are needed for protection of the polymer, and this usually means from 0.2 to 0.5%.

Tinuvin 622, Uvisol 226 and Lowilite 62 are trade-names of the same HAS product with the IUPAC name poly-(*N*- $\beta$ -hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxypiperidyl succinate). This is an oligomer where *n* is assumed to be 2–14, whereas the majority of the product is believed to be 11–14. The average molecular weight is reported to range

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from 3100 to 4000, which has been determined by the use of size exclusion chromatography (SEC) [2].

Unfortunately, the desire for a HAS product that has low volatility and extractability, makes it difficult to analyze it by conventional gas chromatography (GC) or high-performance liquid chromatography (HPLC). In both techniques it has been necessary, prior to the analysis, to derivatize with tetrabutylammonium hydroxide (TBAH), and thereby producing small molecular units (MW=200) which are more convenient for the above mentioned techniques [3]. Unfortunately this procedure yields little or no information about the oligomer distribution.

The analytical techniques previously used do not give any information of the oligomer distribution or of possible isomers in the trade product. The manufacturers of polypropylene and polyethylene need more information of the products particularly concerning the oligomer distribution. Also there is a desire to be able to compare products from different manufacturers. With the present commercially available analytical tools, this has been difficult.

Temperature programmed liquid chromatography with the use of relatively long packed capillary columns and non-aqueous mobile phases, was originally developed for the purpose of analyzing polymers, polymer additives, resins in crude oil and other high molecular weight compounds [4]. In a previous paper we have successfully used this method for the analysis of another HAS compound [5]. In this present paper, samples of a HAS-additive produced by three different manufacturers (Tinuvin 622 from Ciba Speciality Chemicals, Lowilite 62 from Great Lakes Chemical Corp. and Uvisol 226 from Uvisol), have been separated for a comparison of their molecular weight distributions by the use of packed capillary temperature programmed liquid chromatography and a modified evaporative laser light scattering detector.

## 2. Experimental

### 2.1. The HTLC-ELSD instrument

The experimental set-up consisted of a Merck

LaChrom L-7100 pump (Merck KGaA, Darmstadt, Germany), a Valco model C4 manual operated injection valve equipped with 50 nl internal loop volume (Valco Instruments, Houston, TX, USA), and a HP 5790 gas chromatograph (Hewlett-Packard, Cupertino, CA, USA) as column oven. A linear fused-silica restrictor (20  $\mu\text{m}$  I.D., 375  $\mu\text{m}$  O.D., approximately 50 cm long) was used as the detector capillary to prevent the mobile phase from boiling. This capillary was fixed 0.2 mm inside the outer nebulizer tubing in the homemade nebulizer [6]. The homemade nebulizer was placed inside a Mark III evaporative laser light-scattering detector (ELSD) (Varex, Alltech Deerfield II, USA) [7]. The mobile phase reservoir was covered with a small constant flow of helium gas to avoid oxygen from entering the mobile phase. All fused-silica capillaries used in this work came from Polymicro Technologies, (Phoenix, AZ, USA).

### 2.2. Column and mobile phase

The column was made out of fused-silica capillary (I.D.=320  $\mu\text{m}$ , O.D.=435  $\mu\text{m}$ ) filled with porous Hypersil ODS (3  $\mu\text{m}$ ) particles from Hypersil, Shandon, UK, according to a procedure described elsewhere [4]. All mobile phase solvents were of HPLC-quality and they were filtered through a 2  $\mu\text{m}$  in-line solvent filter (Upchurch Scientific, Oak Harbor, WA, USA). The mobile phase contained a mixture of triethylamine (Fluka Chemie AS, Buchs, Switzerland) and acetonitrile (SDS, Peypin, France), and the different HAS products were dissolved in mixtures of acetonitrile and toluene (p.a.) from Merck (Darmstadt, Germany).

### 2.3. The HAS compounds

Tinuvin 622 (Ciba Speciality Chemicals, Basle, Switzerland);

Uvisol 226 (Uvisol, Broomen, Switzerland);

Lowilite 62 (Great Lakes Chemical Corp. West Lafayette, Indiana, USA).

All three different trade products were provided by Borealis AS, (Stathelle, Norway).

Tinuvin 622

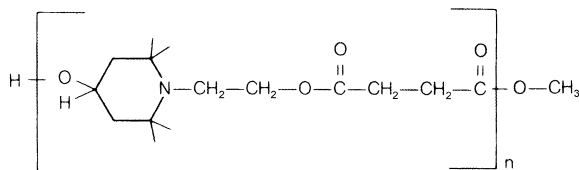


Fig. 1. The HAS compound with the IUPAC name; poly-(*N*-β-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxypiperidyl succinate).

### 3. Results and discussion

#### 3.1. Separation characteristics of the HAS oligomer

This oligomer contains amino groups, which may give irreversible adsorption to a reversed-phase material containing residual silanol groups. This can to some extent be avoided by the use of a highly deactivated material or a deactivating agent in the mobile phase. However, sometimes a combination

might be necessary. According to Fig. 1 the nitrogen atom is shielded by four methyl groups in neighboring positions. This gives reason to assume that the activity between the nitrogen atom and the residual silanol groups on the chemical bonded silica surface is restricted. In our preliminary work with these products, we were actually able to characterize two of these products without using a deactivating agent, relatively satisfactorily. However, by using triethylamine as a deactivating agent, not only were we able to fully characterize all three products, but also the reproducibility of retention times were significantly improved. Another relatively similar HAS compound that contained several unshielded amino groups, required the use of a deactivating agent (triethylamine) in the mobile phase [5] for all products evaluated.

As can be seen from the different chromatograms (Figs. 2–4), the total number of peaks that can be observed is approximately 50. Although this is not yet established with certainty, the number of monomeric units appears to be significantly higher than what has been suggested from the different manufac-

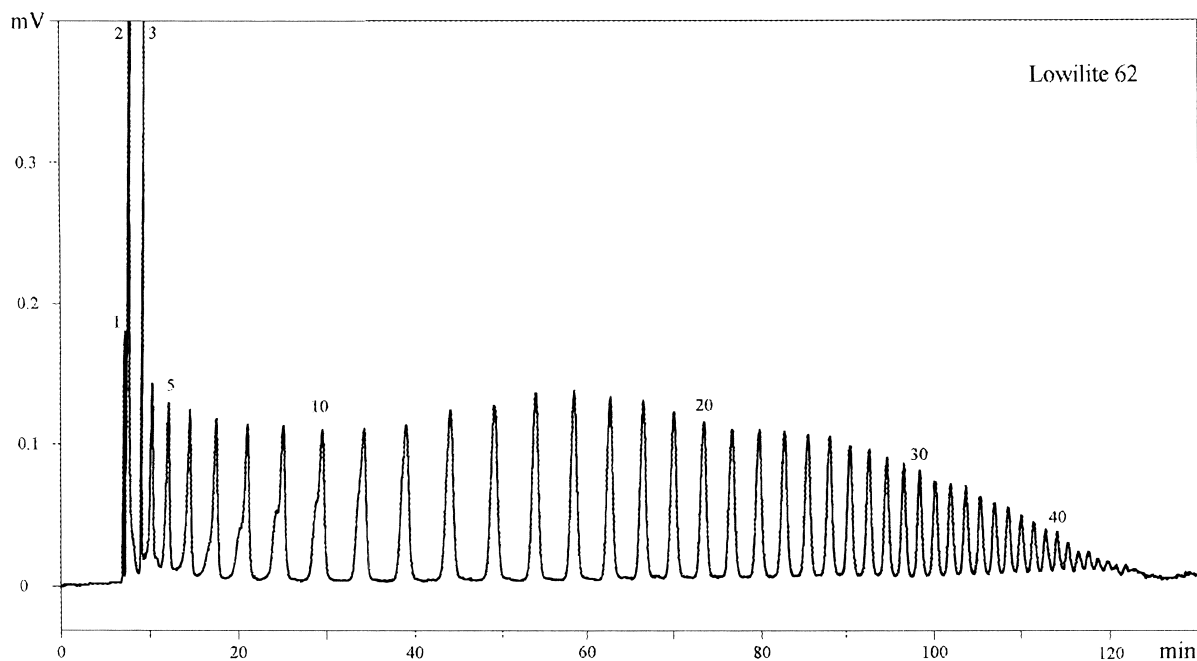


Fig. 2. 20 mg/ml Lowilite 62 (dissolved in 20% toluene+80% acetonitrile v/v) analyzed by the use of light scattering detection. The column was; 0.32 mm×40 cm packed with 3 μm Hypersil ODS particles, and 95% acetonitrile+5% triethylamine v/v was used as mobile phase. Flow=3 μl/min. T-program: 28°C (2 min), then 0.7°C/min to 120°C. Detector: drift tube temperature=90°C and 2.20 SLPM N<sub>2</sub>.

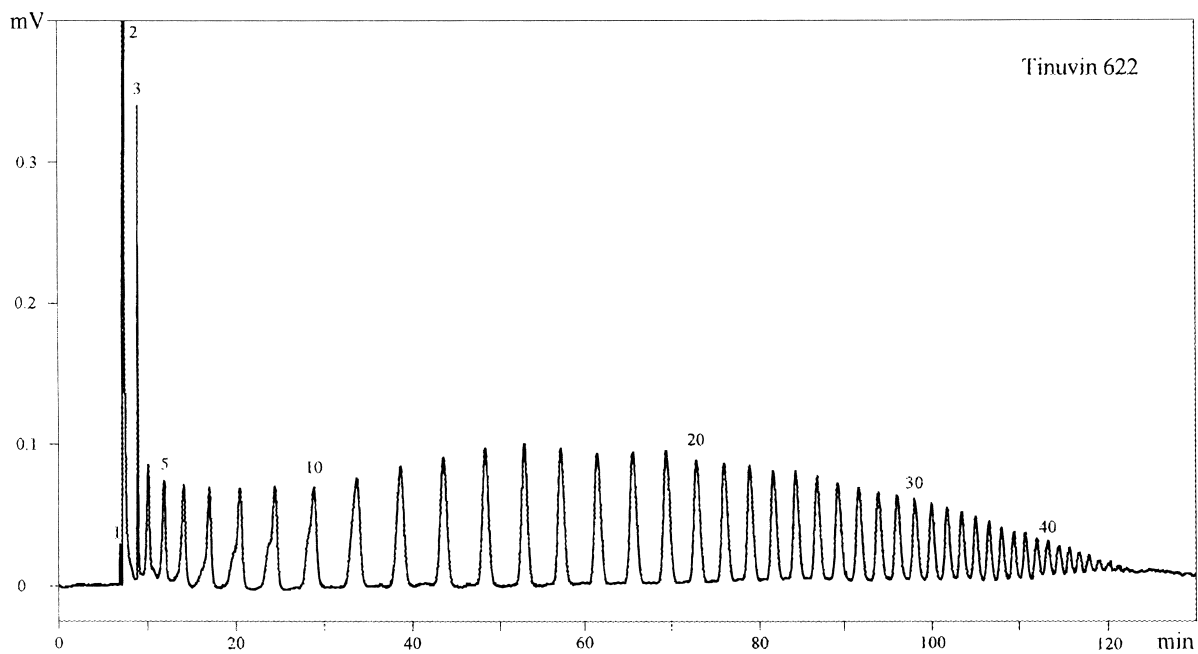


Fig. 3. 20 mg/ml Tinuvin 622. Experimental conditions as in Fig. 2.

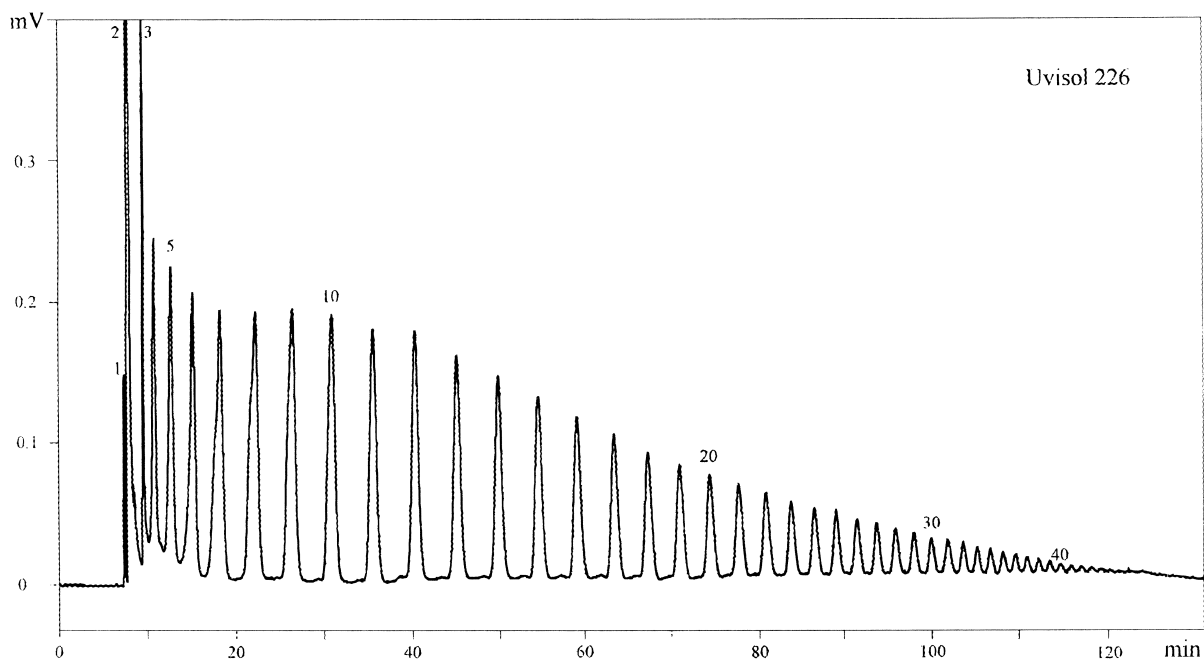


Fig. 4. 20 mg/ml Uvisol 226. Experimental conditions as in Fig. 2.

turers, and the high end of the MW range appears to be in the vicinity of 15000. It appears that all three products are identical, but the product Uvisol 226 (Fig. 4) has a slightly different profile on peaks 5–20, additionally it has less peaks above peak number 40 in contrast to the other product. Based on peak height estimates we therefore suggest that Uvisol 226 has less oligomers in the high MW range than the other two products. We also believe that the apparently distorted peaks in Figs. 2 and 3 (peak nr 7, 8, 9 and 10) are caused by partially resolved components; the “main” product, and a byproduct.

### 3.2. Choice of packing material and particle size

Based on the results with the other HAS compound [5], we also found that reducing the particle size from 5 to 3  $\mu\text{m}$  was crucial. This is attributed to the slow mass transport for these relative high molecular compounds, which necessitated the use of smaller stationary phase particles to improve the separation power. The higher surface area of 3  $\mu\text{m}$  particles may also have facilitated adsorption and focusing at low column temperature. Hypersil ODS was found to be the best stationary phase choice, and this material is known to be the (older) acidic type silica that is now called type A silica, indicating that the residual silanol groups played a role for the retention mechanism.

### 3.3. Temperature, -focusing, -programming and injection solvent

The use of toluene as solvent was necessary for dissolving the HAS compounds at a concentration of 20 mg/ml, which was needed to be able to detect as many peaks as possible using an injection volume of 500 nl. Toluene has a higher elution strength than the mobile phase that was used, which obviously is a source for band broadening. This could be compensated for to some extent by using as low oven temperature as practically possible at the start of the temperature ramp. The use of temperature programming was necessary to be able to separate all the components in the products in a reasonable time, and

Table 1

Retention time reproducibility data. Comparison of the average retention times ( $n=3$ ) for peak number 1, 2, 3, 5, 10, 20, 30 and 40

Peak number	Retention time (min)		
	Tinuvin 622	Uvisol 226	Lowilite 62
1	7.15 $\pm$ 0.08	7.64 $\pm$ 0.60	7.26 $\pm$ 0.16
2	7.49 $\pm$ 0.09	7.97 $\pm$ 0.61	7.56 $\pm$ 0.16
3	9.21 $\pm$ 0.08	9.73 $\pm$ 0.62	9.31 $\pm$ 0.18
5	12.28 $\pm$ 0.12	12.84 $\pm$ 0.64	12.39 $\pm$ 0.20
10	29.59 $\pm$ 0.57	30.34 $\pm$ 0.81	30.03 $\pm$ 0.19
20	73.29 $\pm$ 0.30	73.54 $\pm$ 0.72	73.62 $\pm$ 0.22
30	98.31 $\pm$ 0.41	98.85 $\pm$ 0.87	98.65 $\pm$ 0.26
40	113.53 $\pm$ 0.25	114.07 $\pm$ 0.52	113.83 $\pm$ 0.09

for improving the peak shape for the late eluting compounds.

### 3.4. The use of packed capillary T-programmed LC for purity control

The use of elevated temperature to increase the mass transfer between the mobile and the stationary phase is well known, and the combination of small particles and elevated temperature resulted in the high resolution that can be observed in Figs. 2–4. Additionally, temperature programming enables differentiation between the three commercial products, regarding the total number of components and the quantity of each. Further, Table 1 shows that retention time reproducibility for selected peaks in the chromatograms were highly acceptable.

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## References

- [1] W. Freitag, J. Chromatogr. 450 (1988) 430.
- [2] Private communication from Borealis, Stathelle, Norway.
- [3] Tinuvin 622 LD Determination in polyolefins (product specification from Ciba Speciality Chemicals) KC-158/1.

- [4] R. Trones, A. Iveland, T. Greibrokk, J. Microcol. Sep. 7 (1995) 505.
- [5] R. Trones, T. Andersen, T. Greibrokk, D.R. Hegna, J. Chromatogr. A 874 (2000) 65.
- [6] S. Hoffmann, H.R. Norli, T. Greibrokk, J. High Resolut. Chromatogr. 12 (1989) 260.
- [7] R. Trones, T. Andersen, T. Greibrokk, J. High Resolut. Chromatogr. 22 (1999) 283.