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Hindered amine stabilizers investigated by the use of packed capillary temperature-programmed liquid chromatography I. Poly((6-((1,1,3,3-tetramethylbutyl)-amino)-1,3,5-triazine-2,4-diyl)(2,2,6,6-tetramethyl-4-piperidyl)imino)-1,6-hexanediyl ((2,2,6,6-tetramethyl-4-piperidyl)imino))

Roger Trones[a,*], Thomas Andersen[a], Tyge Greibrokk[a], Dag R. Hegna[b]

[a]*Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, 0315 Oslo, Norway*

[b]*Borealis AS, 3960 Stathelle, Norway*

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Abstract

Three different trademarks of a hindered amine stabilizer with the IUPAC name poly((6-((1,1,3,3-tetramethylbutyl)-amino)-1,3,5-triazine-2,4-diyl)(2,2,6,6-tetramethyl-4-piperidyl)imino)-1,6-hexanediyl((2,2,6,6-tetramethyl-4-piperidyl)-imino)), have been analyzed and compared to each other by the use of non-aqueous packed capillary temperature-programmed liquid chromatography and light scattering detection. The analysis by this method has shown that the products contained almost 40 different homologues and other components. This is in contrast to what has been assumed earlier based on results achieved with size exclusion chromatography. The method demonstrated significant differences between the products from different manufacturers.

Keywords: Hindered amine stabilizers; Temperature programming; Light scattering detection

1. Introduction

It is a well known fact, that degradation (oxidation) of polyolefins like polypropylene (PP) and polyethylene (PE) is accelerated by the presence of UV-light and oxygen. By introducing oligomeric hindered amine stabilizers (HAS) into the polymer, the polymer itself is protected against degradation, and its durability is prolonged as long as the HAS compound is active. The protecting mechanism(s) are not completely understood, but some theories appear in the literature [1,2].

A widely used HAS compound is poly((6-((1,1,3,3-tetramethylbutyl)-amino)-1,3,5-triazine-2,4-diyl)(2,2,6,6-tetramethyl-4-piperidyl)imino)-1,6-hexanediyl((2, 2, 6, 6 - tetramethyl - 4 - piperidyl)imino)). This is an oligomer where n is assumed to be equal to between 1 and 6. The molecular weight (M_w) is reported to range from 2000 to 3100, with an average weight of 2600, which has been determined

*Corresponding author.

E-mail address: roger.trones@kjemi.uio.no (R. Trones)

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by the use of size exclusion chromatography (SEC) [3]. Its melting point range is determined to be 100–130°C. These products are normally present in the polymer at concentrations lower than 1%, and often as low as 0.05%.

Characterization of this oligomer is difficult for several reasons; it has a broad molecular weight distribution, it may contain isomers, and it has several amino groups that promote almost irreversible adsorption to silica-based column packings in liquid chromatography. Chromatographic separations of different HAS trade products (eluted as one peak) that are extracted from polymer matrixes, have been performed with pyrolysis–gas chromatography [4], high-performance liquid chromatography (HPLC) with flame ionization detection [5], UV-detection [6], and size-exclusion HPLC with UV-detection [7].

To our knowledge a very limited number of papers containing chromatographic characterization of the present HAS compound have been published. Polymer extracts of the HAS Chimassorb 944 have been attempted by separation with reversed-phase gradient elution HPLC with UV-detection [8,9] and size-exclusion HPLC with UV-detection [10]. However, these studies have not resulted in any information of the oligomer distribution or possible isomers in the trade product. The manufacturers of polypropylene and polyethylene need more information on the products particularly concerning the oligomer distribution. Also there is a desire to be able to examine the products of different manufacturers. With the present commercially available analytical tools, this has been difficult.

High-temperature liquid chromatography (HTLC) with the use of relatively long packed capillary columns and non-aqueous mobile phases, is an analytical separation technique originally developed for the purpose of analyzing polymers, polymer additives, resins in crude oil and other high molecular weight compounds [11]. In this paper, samples of a HAS-additive produced by three different manufacturers (Chimassorb 944 from Ciba Speciality Chemicals, HALS 94 from Palmerole and Uvisol DL 449 from Uvasil), have been separated for a comparison of their molecular weight distributions by the use of packed capillary HTLC, 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 C4W manual-operated injection valve equipped with a 500-nl internal loop volume (Valco Instruments, Houston, TX, USA), and a Carlo Erba 3000 gas chromatograph (Carlo Erba, Milano, Italy) as a column oven. A linear fused-silica restrictor (20-μm I.D., 375-μm 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 laboratory made nebulizer, due to earlier experiments [12]. The laboratory made nebulizer was placed inside a Mark III evaporative laser light-scattering detector (ELSD) (Varex, Alltech Deerfield IL, USA) [13]. 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. Preparation of columns and mobile phases

All columns were packed in fused-silica capillaries (I.D.=320 μm, O.D.=435 μm) according to the procedure described by Trones et al. [11]. The packing materials used were porous Hypersil ODS [3-μm and Hypersil BDS (5-μm) particles (Hypersil, Shandon, UK) and Kromasil 100 RP18 (5-μm) particles (Shandon Southern Products, Cheshire, UK).

All mobile phase solvents were of HPLC-quality and they were filtered through an in-line solvent filter with 2-μm pores (Upchurch Scientific, Oak Harbor, WA, USA). The mobile phase was ternary mixtures of ethylacetate (Rathburn Chemicals, Walkerburn, UK), acetonitrile (SDS, Peypin, France) and diethylamine/triethylamine (Fluka Chemie AS, Buchs, Switzerland).

2.3. The HAS compounds

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

3. Results and discussion

3.1. Characterization of the HAS oligomer

Separating an oligomeric product that contains homologues and possibly also stereoisomers due to chirality at nitrogen centers is a challenge. If we assume one chiral center, and the maximum number of monomeric units $n=1–6$, the maximum number of components including homologues and isomers will be 126. The smallest homologue ($n=1$) contains at least three possible chiral centers, which makes a huge number of homologues and isomers for $n=1–6$. However, if the inversion movement is not sufficiently restricted, the inversion rate is too high to permit resolution between isomers. A normal inversion rate for aliphatic tertiary amines is 10^3 to 10^5 times per second at room temperature [14], but here we operate at elevated temperature, which means that the inversion rate of a non-restricted amine is probably higher. The fact that the total number of peaks in the different chromatograms is higher than the homologues expected, could indicate that here we are dealing with some isomers that have restricted inversion. However, by comparing the chromatograms of the three trade products, the minor peaks marked Xb–c–d are much smaller in Figs. 2 and 3, compared to the ones in Fig. 1. If the minor peaks were structure isomers based on restricted inversion of one or more chiral amino groups, one would not expect such large height differences between the peaks in the products. Thus, we believe that all the minor peaks in Figs. 1–3 marked Xb–c–d and the ones marked 1x–2x–3x in Fig. 1 more than likely are biproducts caused by competing polymerization reactions or by impurities in the raw materials. The Hals 94 and the Uvisol 446 products appear to be almost identical products, and differ significantly from the Chimassorb 944 product. In our opinion this actually supports our suggestion of a competing polymerization reaction during the syntheses of the different products. Unfortunately, this could not be verified due to the lack of available reference compounds.

3.2. Number of monomeric units

As can be seen from the different chromatograms (Figs. 1–3), the total number of peaks that can be observed (detected) is approximately 40. Although this is not yet established with certainty, the number of monomeric units appears to be significantly higher than the previous methods have indicated. The major peaks in Figs. 1–3 are marked Xa, and the maximum number is approximately 20, and we therefore suggest that the HAS compound contains a minimum of 1–20 monomeric units ($n=1–20$). At the high end this is equivalent to a molecular weight of approximately 9300. We cannot however, with the present detector, exclude the presence of higher monomeric units, but we believe that the majority of the mass is distributed in the range of $n=1–20$. Electrospray FT–ICR mass spectrometry has indicated that $n>6$ [15], but since only the major ions are seen, LC–MS will be needed to confirm these findings. The earlier suggestion of $n=1–6$ was based on SEC, and the fact that the highest and quantitatively largest peaks in our chromatograms are smaller than '$n=10$' is actually in agreement with this. SEC is, after all, a method not known for its accuracy, and there are no reference compounds available.

As can be seen by comparing the chromatograms from the different trade products, temperature programming enables differentiation between the three commercial products, regarding the total number of components and the quantity of each component.

3.3. Injection volume and temperature programming

All injections were performed with a 500-nl injection volume. This was necessary to be able to detect as many of the different compounds as possible at the high end of the M_w range. A smaller injection volume requires the use of higher concentrations to achieve the same detection. This would increase the possibility of injection of particulates, with damage to the injector as result. Injecting 500 nl on a 0.32-mm I.D. packed capillary column is not recommended in the literature [16], unless a solute focusing technique is involved. However, we did not experience significant detrimental effects from the use of 500-nl injections, and we suggest that the reason for this can be partly

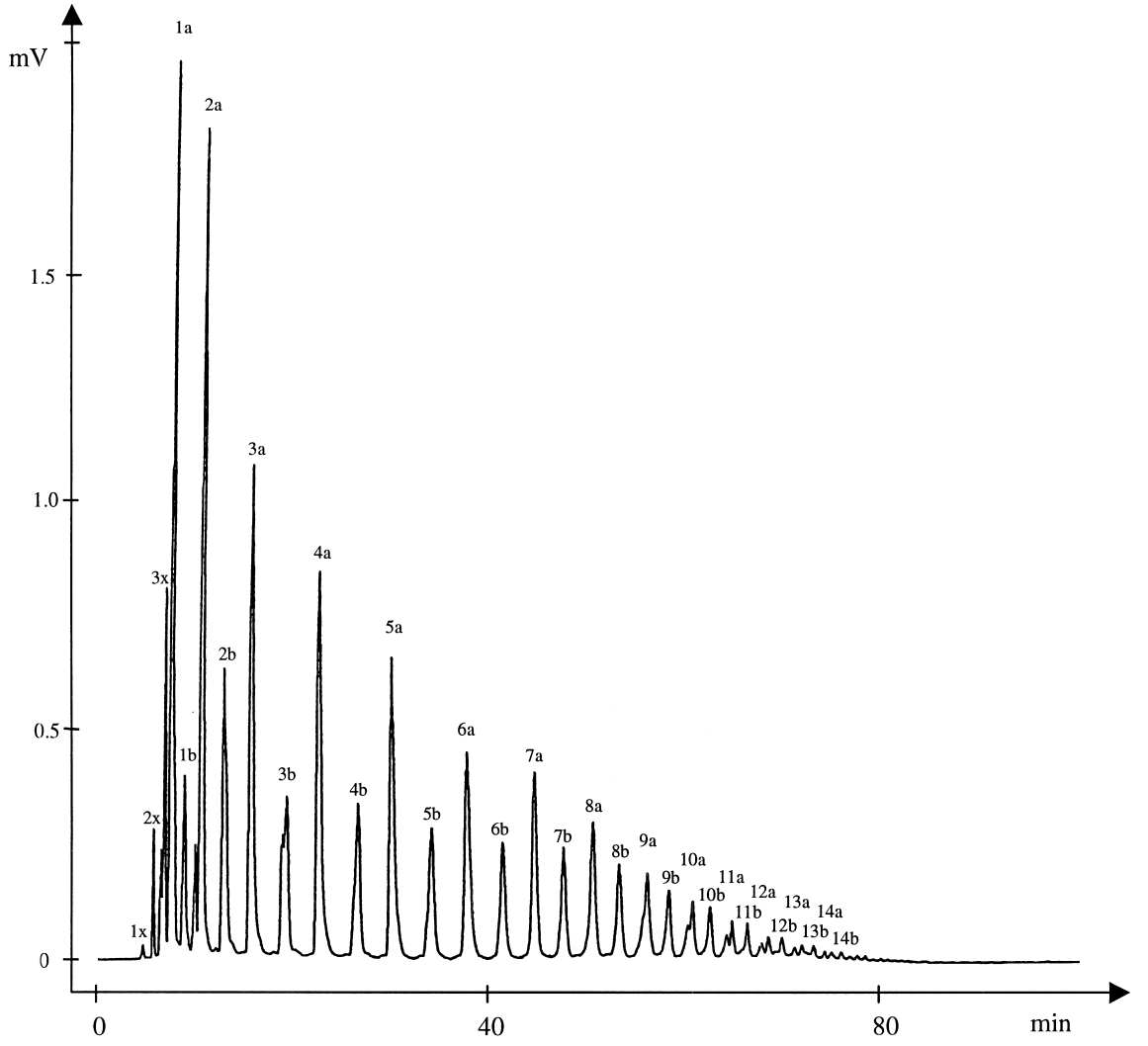

Fig. 1. 10 μg Chimassorb 944 (dissolved in mobile phase) analyzed by the use of light-scattering detection. The column was; 0.32 mm×35 cm packed with 3-μm Hypersil ODS particles, and ethylacetate–acetonitrile–triethylamine (40:50:10) was used as mobile phase. Flow=5 μl/min. *T*-program: 30°C (6 min), then 1°C/min to 130°C. Detector: drift tube temperature=95°C and 2.25 SLPM N_2. The Xa numbers indicate the assumed main units in the oligomer. lx–2x–3x and Xb–c–d are assumed to be byproducts or impurities.

attributed to the use of a temperature gradient which is believed to act similarily to a mobile phase gradient.

3.4. Packing materials and particle size

As can be seen in Fig. 4, the oligomer contains several amino groups, which makes it necessary to either use a highly deactivated reversed-phase material or a deactivating agent in the mobile phase. This is due to the activity of the stationary phase's residual silanol groups towards amino groups, which may give irreversible adsorption. In some cases, however, it may be necessary to use a combination. Our choice of deactivating agents; triethylamine and diethylamine gave similar chromatographic performance, but triethylamine gave the best signal-to-noise ratio for the light-scattering detection.

In contrast to Caceres et al. which separated different HAS [17], we found that the C_{18} material

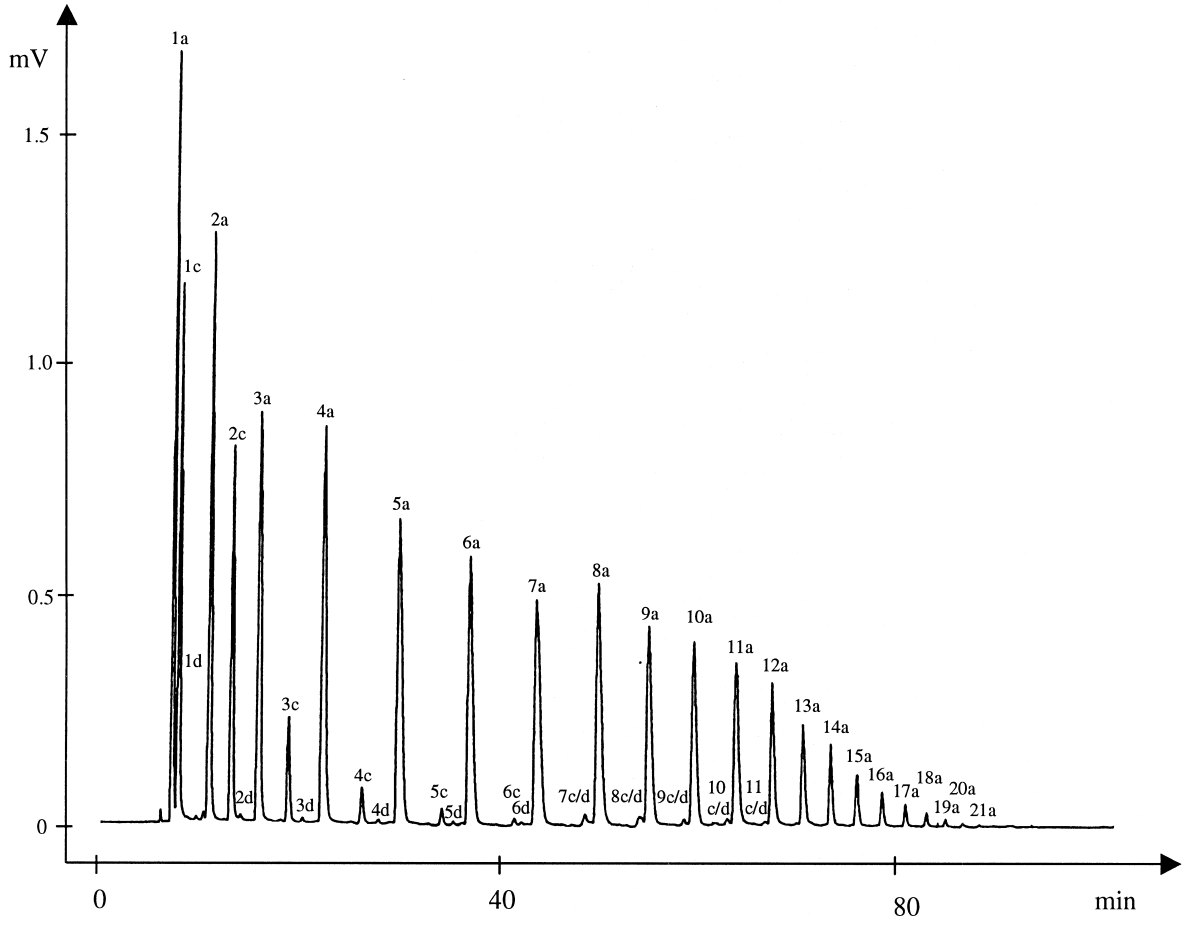

Fig. 2. 10 μg HALS 94 (dissolved in mobile phase) analyzed by the use of light-scattering detection. The column was: 0.32 mm×35 cm packed with 3-μm Hypersil ODS particles, and ethylacetate–acetonitrile–triethylamine (40:50:10) was used as mobile phase. Flow=5 μl/min. *T*-program: 30°C (6 min), then 1°C/min to 130°C. Detector: drift tube temperature=95°C and 2.25 SLPM N_2. The Xa numbers indicate the assumed main units in the oligomer. Xb–c–d are assumed to be byproducts or impurities.

was well suited as a separation medium, and we evaluated one type-B silica; Kromasil RP-18, base deactivated silica; Hypersil BDS (both 5 μm), and type A silica (Hypersil ODS 3-μm and 5-μm particles). Among the materials available as 5-μm particles, Kromasil RP-18 was the best choice, but the particle diameter was more important, resulting in improved performance with 3-μm Hypersil ODS. Hypersil ODS is known to be the (older) acidic type silica that are now called type A silica, indicating that the rest-silanol groups may play a role for the retention mechanism. The higher surface area of 3-μm particles may also have facilitated adsorption and focusing at low column temperature. 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. 1–3.

Based on preliminary results with the use of 70-cm long columns and 5-μm particles, we found that reducing the column length to 40 cm and the particle size down from 5 to 3 μm was crucial. Extending the length of columns with 5-μm particles up to 150 cm did not improve the analysis sufficiently compared to the use of the shorter ones with 3-μm particles. This is attributed to the relative slow mass transport for these relatively high molecular compounds which

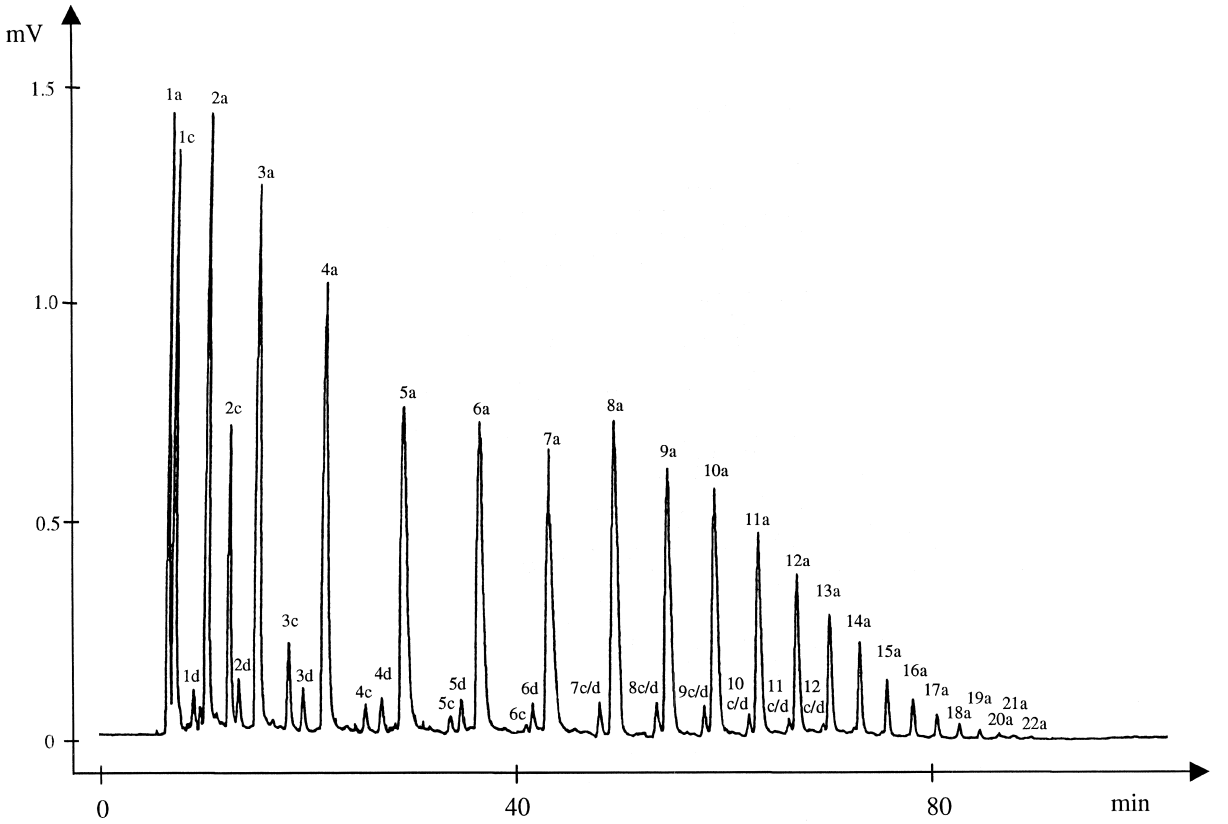

Fig. 3. 10 μg Uvisol DL 449 (dissolved in mobile phase) analyzed by the use of light-scattering detection. The column was; 0.32 mm×35 cm packed with 3-μm Hypersil ODS particles, and ethylacetate–acetonitrile–triethylamine (40:50:10) was used as mobile phase. Flow=5 μl/min. *T*-program: 30°C (6 min), then 1°C/min to 130°C. Detector: drift tube temperature=95°C and 2.25 SLPM N_2. The Xa numbers indicate the assumed main units in the oligomer. Xb–c–d are assumed to be byproducts or impurities.

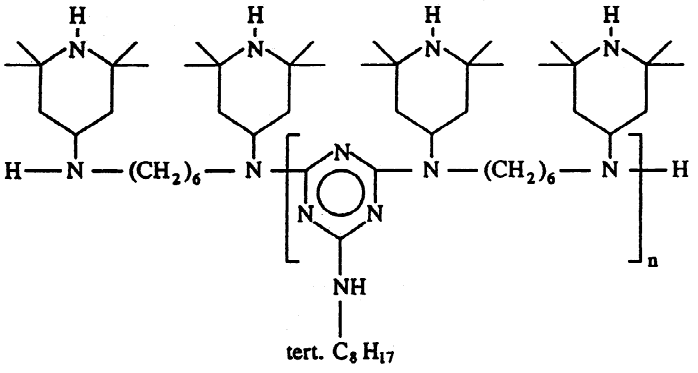

Fig. 4. The structure of the HAS compound with the IUPAC name; poly((6-((1,1,3,3-tetramethylbutyl)-amino)-1,3,5-triazine-2,4-diyl)(2,2,6,6-tetramethyl-4-piperidyl)imino)-1,6-hexanediyl((2,2,6,6-tetramethyl-4-piperidyl)imino)).

necessitated the use of smaller stationary phase particles for improving the separation power.

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