Chapter 11

# Identification of Some New Generation Additives for Polymers Obtained in the Catalytic Hydrogenation Process

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Additional information is available at the end of the chapter

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**Abstract**

The identification of new generation additives such as plasticizers and hardeners applied mainly to some polymers and resins and obtained in the catalytic hydrogenation processes is presented. The new plasticizers di(n- and isononyl)cyclohexane-1,2-dicarboxylates (DINCH) were obtained by catalytic hydrogenation of the planar aromatic rings of the mixture of di(alkyl($C_9$))phthalates in the presence of the modified Ni catalyst. They may be used as a substitute for improving the flexibility of polymers, such as PVC, and also for strongly reducing the toxic effects on human health of the 1,2-di(alkyl)phthalates, which is easily released from the polymer to the environment. The identification of these types of compounds by GC/MS enables to determine the structures of the main products such as *cis* and *trans* isomers of the cyclohexane-1,2-dicarboxylates. GC/MS may be applied to the identification of some DINCH constituents extracted from polymers. Also, the analysis of these compounds by ESI/MS gives information about their mass fragmentation and enables their detection, although without differentiation between individual *cis* and *trans* isomers.

Branched poly(amines) may be used as the cross-linking agents for the most effective crosslinking of the epoxy resins. Final product from the synthesis of the poly(amines) may be easily analyzed by GC/MS and spectroscopic techniques.

**Keywords:** hydrogenation, identification, plasticizers, di(n- and isononyl)cyclohexane-1,2-dicarboxylates, hardeners, branched poly(amines)

## 1. Introduction

Di(n- and isononyl)cyclohexane-1,2-dicarboxylate (DINCH) isomers are considered to be relatively safe substitutes of the corresponding phthalates, especially when used in the manufacturing of various medical devices and toys. For this reason there is a great interest in the analysis of their isomers by different analytical methods.

In this chapter, we present the results of the application of the different modern chromatographic and spectrometric analytical techniques, such as gas chromatography (GC), electrospray-mass spectrometry (ESI/MS), Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), gas chromatography-mass spectrometry (GC/MS), and others similar ones to the identification of the new generation additives.

They were obtained in the catalytic hydrogenation reactions in the presence of the Ni catalyst and used as plasticizers and cross-linking agents to some polymers, such as poly(vinyl chloride) (PVC) or epoxy resins.

## 2. Plasticizers

### 2.1. Di(alkyl)cyclohexane-1,2-dicarboxylates

Di(alkyl) esters of 1,2-benzene dicarboxylic acid of higher molecular weight, such as di(2-ethylhexyl)phthalate (DEPH) or di(isononyl)phthalate (DINP), are widely used as plasticizers in the processing of various types of polymers, especially poly(vinyl chloride). These types of compounds are not chemically bound to the polymers, so they are gradually released from them by volatilization from the surface into the air, or by migration due to contact with a solid, or by extraction from the polymer into a liquid also due to direct contact [1]. These compounds are becoming challenging environmental pollutants with a strong impact on the human health. The toxicity effects of these compounds have been intensively investigated, and within the last decade some of those compounds have been classified as endocrine disruptors [2] and potential carcinogens [3–6]. The metabolism of DINP in animals [7] and in humans [8, 9] has been studied. In these studies, where deuterium-labeled DINP was used, samples of animal and human urine were found to contain monoester of mono-iso-nonylphthalate and its oxidized isomers containing hydroxy, oxo, and carboxy functional groups as metabolites of DINP.

The new di(alkyl)cyclohexane 1,2 dicarboxylates (DINCH) plasticizers may be used to improve the flexibility of some polymers, mainly PVC. They also have less toxic effect on human health when compared to di(alkyl)phthalates.

### 2.2. Synthesis of di(n- and isoalkyl($C_4$–$C_9$))cyclohexane-1,2-dicarboxylates

Cyclohexanedicarboxylic esters are produced through the catalytic hydrogenation of corresponding phthalates or through the Diels-Alder reaction of maleic acid esters with ethylene followed by hydrogenation using supported nickel catalyst [10].

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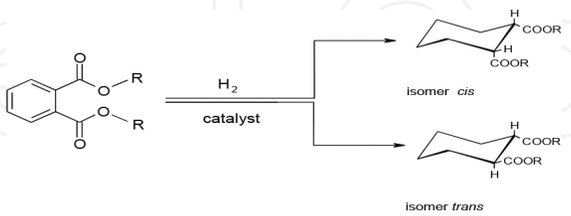
Di(n- and isoalkyl($C_4$–$C_9$)) phthalates were synthesized in the esterification reaction of phthalic anhydride with appropriate aliphatic alcohol using an optimized procedure [11, 12]. Hydrogenation of these esters, after their prior purification by distillation, were carried out in a high pressure reactor in the presence of the Ni catalyst on aluminosilicate support at 150°C for 3.0 h and under 9.0 MPa hydrogen pressure, according to the following scheme:




where R = alkyl (C4 – C9).

During the hydrogenation reaction of di(alkyl)phthalates, *cis* and *trans* isomers of the di(alkyl($C_4$–$C_9$))cyclohexane-1,2-dicarboxylates are formed as the main products with a yield of 98.0%.

### 2.3. Identification of di(n- and isoalkyl($C_4$–$C_9$))cyclohexane-1,2-dicarboxylates

Identification of *cis* and *trans* isomers of the synthesized di(n- and iso-nonyl)cyclohexane-1,2-dicarboxylates was done by chromatographic and spectrometric methods of GC/MS and ESI/MS.

#### *2.3.1. GC/MS analysis*

Chromatographic separation of the compounds investigated and registration of their "electron impact" mass spectra (EIMS) was done by use of a gas chromatograph HP 6890 Series GC System (Hewlett-Packard, Palo Alto, CA, USA) equipped with HP 5973 Network quadrupole mass selective spectrometric detector (Agilent Technologies, Palo Alto, CA, USA). Each sample was dissolved in $CHCl_3$ to 5,0% solution. Then 0.1 μL of that solution was injected by using Hamilton microsyringe to the split/splitless injector (split mode 100:1) kept at 350°C. The fused silica capillary column HP 50+ (30.0 m length, internal diameter 0.2 mm and 0.2 μm phase film thickness) was heated in the range of 70–290°C with programmed temperature ramp 7°C/min. As a carrier gas helium (ultra-pure, 99,999%) was used.

GC/MS was applied to analyze the synthesized *cis* and *trans* isomers of di(n- and isononyl) esters of 1,2-cyclohexanedicarboxylic acid in order to get their good chromatographic separation enabling to record their electron impact (EI) mass spectra and also to calculate their arithmetic retention indices $I_A$ on the basis of their retention times $t_r$.

**Figure 1** shows an example of a chromatogram of *cis* (compound $a_1$) and *trans* (compound $a_2$) of the di(3,5,5-trimethylhexyl) esters of cyclohexane-1,2-dicarboxylic acid as the reaction products of di(3,5,5-trimethylhexyl)phthalate hydrogenation. Values of the retention times $t_r$

of the *cis* and *trans* isomers of the esters are always lower than those of the corresponding phthalates.

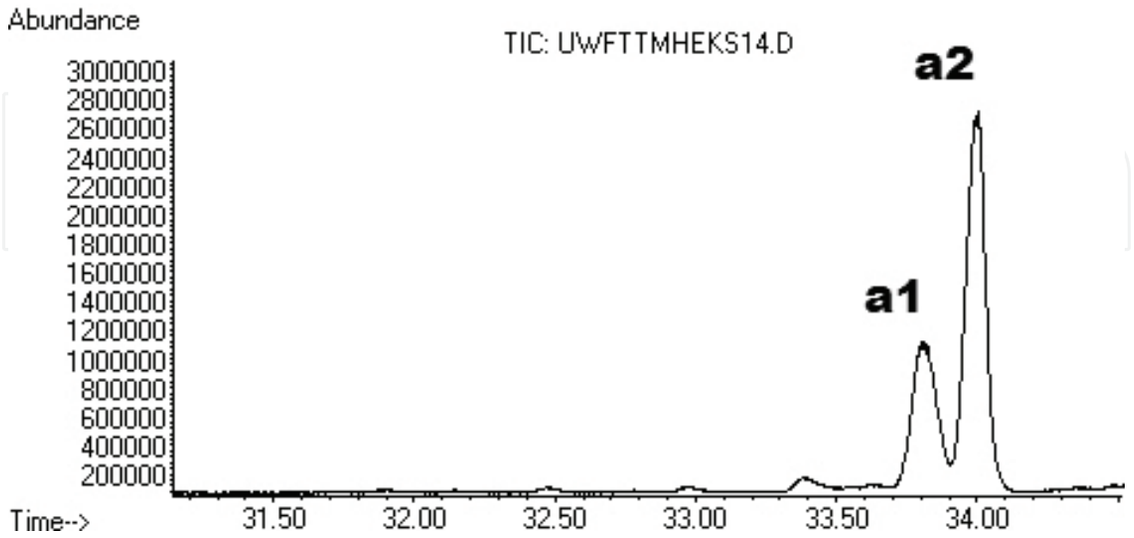



**Figure 1.** GC/MS chromatogram of *cis* ($a_1$) and *trans* ($a_2$) isomers of di(3,5,5-trimethylhexyl)cyclohexane-1,2-dicarboxylate.

On the basis of the retention times $t_r$ of all analyzed *cis* and *trans* isomers and the retention times of a standard mixture of *n*-alkanes $C_{20}$–$C_{40}$, the arithmetic retention indices ($I_A$) were calculated using the following formulae (1) [13]:

$$I_A = 100z + 100\frac{T_i - T_z}{T_{z+1} - T_z} \tag{1}$$

where $T_i$, $T_z$, and $T_{z+1}$ are the retention times of the analyzed component and neighboring *n*-alkanes containing $z$ and $z + 1$ carbon atoms, wherein $T_z < T_i < T_{z+1}$

The obtained values of $I_A$ for the analyzed compounds are given in **Table 1**.

The linear relationship was found between the values of arithmetic retention indices $I_A$ of di(n-alkyl($C_4$–$C_9$))phthalates and the number of carbon atoms present in the alkyl substituents of esters obtained during the hydrogenation of appropriate phthalates [12].

The values of $I_A$ of di(n-alkyl($C_4$–$C_9$)) phthalates are higher than those of their hydrogenation products. In both cases there is also a regularity according to which the esters with the longer alkyl substituents have the greater values of the arithmetic retention indices $I_A$. Whereas in the case of the esters with branched alkyl chains of the substituents, their retention times $t_r$ and arithmetic retention indices $I_A$ have lower values compared to those of the corresponding esters with straight chain substituents. The values of their retention times are

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arranged in the following order: $t_{ra1,a2} < t_{rb1,b2} < t_{rc1,c2}$ and, similarly, the arithmetic retention indices are arranged in the following order: $I_{A1,A2} < I_{B1,B2} < I_{C1,C2}$.

The obtained $t_r$ and $I_A$ reference GC parameters for the analyzed *cis* and *trans* isomers of the di(n- and isononyl)cyclohexane-1,2-dicarboxylates can be used for the unambiguous determination of the chemical structure of this type of organic compounds, particularly when both are present in the reaction product of the hydrogenation of di(n- and isononyl)phthalic acid esters. They may also be very useful for ongoing optimization of the technological parameters of the hydrogenation process using only the GC method.

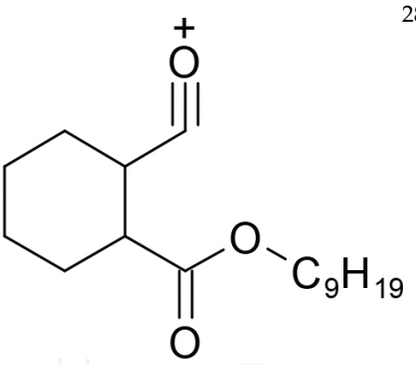
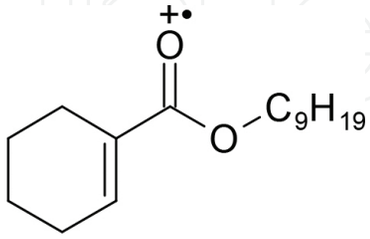
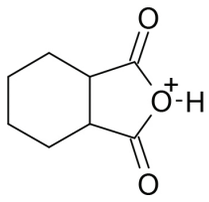
| Compound | Name of compound | Mol. weight [g/mol] | Retention time, $t_r$ [min] | Arithmetic retention index, $I_A$ |
|---|---|---|---|---|
| $a_1$ | Di(3,5,5-trimethylhexyl)cyclohexane-1,2-dicarboxylic acid (*cis* isomer) | 424 | 33.81 | 2780.0 |
| $a_2$ | Di(3,5,5-trimethylhexyl)cyclo-hexane-1,2-dicarboxylic acid (*trans* isomer) | 424 | 34.00 | 2798.1 |
| *A* | Di(3,5,5-trimethylhexyl)phthalate | 418 | 35.94 | 2976.9 |
| $b_1$ | Di(2-methyloctyl)cyclohexane-1,2-dicarboxylic acid (*cis* isomer) | 424 | 34.51 | 2846.7 |
| $b_2$ | Di(2-methyloctyl)cyclohexane-1,2-dicarboxylic acid (*trans* isomer) | 424 | 34.68 | 2862.9 |
| *B* | Di(2-methyloctyl)phthalate | 418 | 37.05 | 3067.5 |
| $c_1$ | Di(n-nonyl)cyclohexane-1,2-dicarboxylic acid (*cis* isomer) | 424 | 37.14 | 3074.6 |
| $c_2$ | Di(n-nonyl)cyclohexane-1,2-dicarboxylic acid (*trans* isomer) | 424 | 37.33 | 3089.7 |
| *C* | Di(n-nonyl)phthalate | 418 | 39.85 | 3257.6 |

**Table 1.** Retention times $t_r$ and arithmetic retention indices $I_A$ of di (n- and iso-nonyl)cyclohexane-1,2-dicarboxylates.

The good chromatographic separation in the GC/MS analysis of the *cis* and *trans* isomers of di(n- and isononyl)cyclohexane-1,2-dicarboxylates enabled recording of their low-resolution EI mass spectra, which are different for each isomer, and as such could be used for unambiguous identification of their chemical structures.

**Table 2** gives the relative intensities of the most characteristic peaks of the molecular and fragment ions of all analyzed *cis* and *trans* isomers of di(n- and isononyl)cyclohexane-1,2-dicarboxylates. In all mass spectra of these isomers there are low intensity peaks of their molecular ions $[M]^{+\bullet}$ present at *m*/*z* 424, which allow to unambiguously determine the molecular weights of these compounds. Also, their mass spectra have a number of peaks referring to the characteristic fragment ions. The most intense characteristic peak of the fragmentation ion is easily recognized in the mass spectra of all analyzed esters (except

the *cis* and *trans* isomers of di(3,5,5-trimethylhexyl)cyclohexane-1,2-dicarboxylates—compounds $a_1$ and $a_2$). It occurs at *m/z* 155 and corresponds to the structure of the protonated anhydride of cyclohexane-1,2-dicarboxylic acid [11, 12]. However, in the mass spectra of the *cis* and *trans* isomers of compounds $a_1$ and $a_2$, in which isoalkyl substituents are more branched, as compared to other isomers—compounds $b_1$, $b_2$, $c_1$, and $c_2$ (**Tables 1** and **2**), the main peak corresponding to the ion at *m/z* 57 has the structure of $[C(CH_3)_3]^+$. It is formed as a result of a homolytic cleavage of the single C–C bond located at the branched carbon atom of the alkyl substituent. The cleavage of the weaker C–C bond occurs more easily than in the other molecular ions $[M]^{+\bullet}$ of the *cis* and *trans* isomers of the esters investigated, and it is the reason of the formation of the less intense ion at *m/z* 155 (also formed from the $[M-{}_9H_{19}]^+$ ion as a result of the elimination of alkoxy radical $^\bullet OC_9H_{19}$ from the molecular ion $[M]^{+\bullet}$ of these compounds). In general, the peak at *m/z* 155 may be used as a diagnostic peak for the unique identification of such type of esters, similarly as the peak at *m/z* 149, the main ion peak of di(alkyl)phthalates (except di(methyl)phthalate). The ion at *m/z* 149 has the structure of the protonated anhydride of phthalic acid [14–16].

| Fragment ion | *m/z* | Relative intensities of fragment ions (%) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Isomer *cis* $a_1$ | Isomer *trans* $a_2$ | Isomer *cis* $b_1$ | Isomer *trans* $b_2$ | Isomer *cis* $c_1$ | Isomer *trans* $c_2$ |
| $[M]^{+\bullet}$ | 424 | 0.01 | 0.19 | 0.07 | 0.04 | 0.09 | 0.28 |
|  | 281 | 11.20 | 4.35 | 3.28 | 3.62 | 20.74 | 9.88 |
|  | 252 | 0.42 | 3.47 | 0.03 | 0.23 | 1.18 | 10.00 |
|  | 155 | 49.83 | 5.70 | 100.00 | 100.00 | 100.00 | 100.00 |

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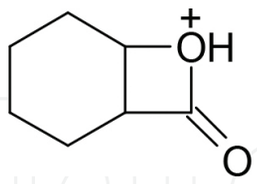
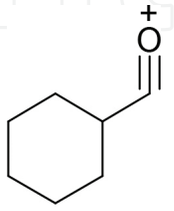
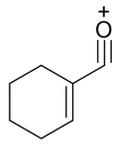
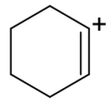
| Fragment ion | *m/z* | Relative intensities of fragment ions (%) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Isomer *cis* $a_1$ | Isomer *trans* $a_2$ | Isomer *cis* $b_1$ | Isomer *trans* $b_2$ | Isomer *cis* $c_1$ | Isomer *trans* $c_2$ |
|  | 127 | 18.95 | 8.16 | 6.70 | 6.41 | 17.89 | 9.80 |
|  | 111 | 9.31 | 11.80 | 0.77 | 0.97 | 0.76 | – |
|  | 109 | 11.30 | 10.41 | 12.97 | 12.82 | 23.06 | 19.83 |
| $[C_6H_{13}]^+$ | 85 | 2.02 | 1.81 | 7.02 | 7.17 | 6.53 | 6.59 |
|  | 81 | 16.64 | 7.00 | 19.59 | 18.93 | 29.40 | 29.60 |
| $[C_4H_9]^+$ | 57 | 100.00 | 100.00 | 13.60 | 15.39 | 16.68 | 16.80 |
| $[C_3H_7]^+$ | 43 | 15.24 | 15.22 | 26.63 | 28.98 | 37.79 | 39.07 |

**Table 2.** Relative ion intensities [A1] of *cis* and *trans* isomers of di(n- and iso-nonyl)cyclohexane-1,2-dicarboxylates in their mass spectra.

Other peaks present in all the MS spectra of the analyzed *cis* and *trans* isomers—compounds $a_1$, $a_2$, $b_1$, $b_2$, $c_1$, and $c_2$—correspond to the characteristic fragment ions formed by the cleavage of single C—C and CO bonds of their molecular ions $[M]^{+\bullet}$. These fragmentation reactions are accompanied by the transfer of hydrogen atoms in the McLafferty rearrangement together with an elimination of the neutral molecules of $H_2O$ and CO (**Table 2**).

**Figures 2a** and **2b** show the mass spectra of isomers *cis* and *trans* of di(3,5,5-trimethylhexyl)cyclohexane)-1,2-dicarboxylic acid.

The differences between EI mass spectra observed in all the analyzed compounds result both from different structures of the alkyl substituents of carboxyl groups of cyclohexane-1,2-dicarboxylic acids and from *cis* and *trans* isomerization being the result of the presence of cyclohexane ring in these esters.

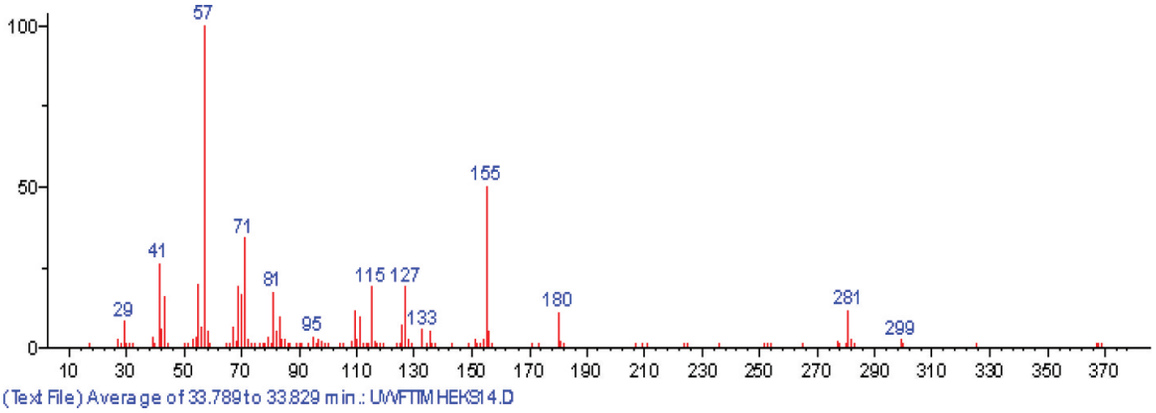



**Figure 2a.** Mass spectrum of compound $a_1$ (**Figure 1**): di(3,5,5-trimethylhexyl)cyclohexane-1,2-dicarboxylate – *cis* isomer.

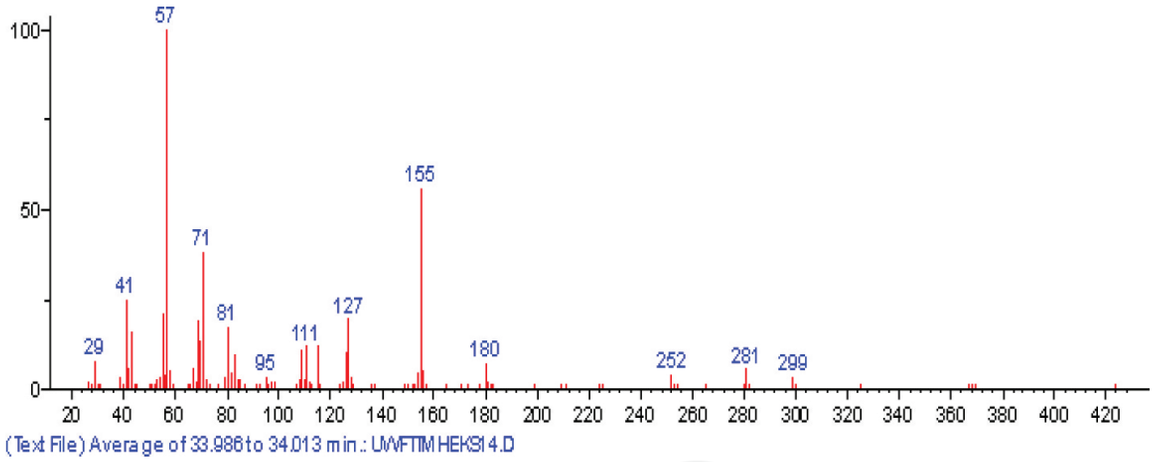



**Figure 2b.** Mass spectrum of compound $a_2$ (**Figure 1**) di(3,5,5-trimethylhexyl)cyclohexane-1,2-dicarboxylate – *trans* isomer.

### *2.3.2. ESI/MS analysis*

Electrospray ionization, being a "soft" ionization technique, was used in mass spectrometry (ESI/MS) for the identification of volatile samples of di(3,5,5-trimethylhexyl)-, di(2-methyloctyl)-, and di(n-nonyl)cyclohexane-1,2-dicarboxylates. Each ESI mass spectrum of the compound investigated represents a mixture of *cis* and *trans* isomers of the same compound, and for this reason it cannot be used for their individual identification.

In ESI/MS analysis the samples of di(n- and isononyl)cyclohexane-1,2-dicarboxylates were dissolved in methanol (HPLC grade, J.T. Baker) and diluted with the same solvent to 1:40,000 (which corresponds to ca. 10 μM). All measurements were performed on an AB

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Sciex Q-TRAP® 4000 series hybrid quadrupole mass spectrometer equipped with electrospray ion source. Collision gas was nitrogen at the nominal pressure $3.2 \times 10^{-5}$ Torr.

The typical ESI mass spectrum of these compounds is shown in **Figure 3**. It presents a mixture of the fragment ion peaks of *cis* and *trans* isomers of di(3,5,5-trimethylhexyl)cyclohexane-1,2-dicarboxylates and only has fewer peaks of mass fragmentation ions in comparison with the individual EI mass spectra (**Figures 2a** and **2b**).

In all the ESI mass spectra of these types of compounds, the peaks of quasi-molecular ions $[M+H]^+$ are present at *m*/*z* 425 and they are formed by the addition of hydrogen cation. They arise from both *cis* and *trans* isomers. More information about the fragment ions could be obtained from the interpretation of ESI mass spectra in which they derived from mass transitions: from $[M+H]^+$ ions at *m*/*z* 281, after the cleavage of one of the unbranched or branched alkyl($C_9$) substituents and following neutral loss of $H_2O$ molecule leading to a fragment ion of *m*/*z* 155. The first transition is the most sensitive, and therefore it may be used to quantify di(n- and isononyl)cyclohexane-1,2-dicarboxylates. The second transition was used only to confirm the results of the first one.

The choice of selected characteristic ions for this type of compounds, for example, with an *m*/*z* of 155, present in other MS spectra of di[n- and isoalkyl($C_4$–$C_9$)]cyclohexane-1,2-dicarboxylates, may be very helpful for their detection during ESI/MS analysis of one or more of the investigated compounds in complex matrices (e.g., PVC) and may also be very useful for quantitative assessment of the level of their actual impact on the human health.

**Figure 4** shows a general mass fragmentation scheme of molecular ions $[M]^+$ of di(n- and isononyl)cyclohexane-1,2-dicarboxylates developed on the basis of the data obtained from their mass transitions. It describes a specific type of fragmentation reactions for this type of compounds as contrasted to the phthalic acid esters. The basic knowledge about their behavior during ionization of this type of compounds will make the interpretation of their mass spectra easier and will enable optimization of the methods of their quantification during the analysis of their release from polymers.

The good chromatographic separation during GC/MS analysis of *cis* and *trans* isomers of di(n- and isononyl)cyclohexane-1,2-dicarboxylates investigated enables the recording of their low-resolution EI mass spectra, which are different from each other and thus can be used for unambiguous identification of their individual chemical structures. Also, chromatographic data, such as the values of retention times $t_r$ and arithmetic retention indices $I_A$, are very useful in their identification, even when the reference substances are not available. The ESI/MS mode was shown to be successful in the determination of *cis* and *trans* isomers of the analyzed esters present in complex matrices of a polymer.

The presented GC, GC/MS, and ESI/MS results for the representatives of the *cis* and *trans* isomers of some of the DINCH group of compounds may also be helpful in the determination of the chemical structures of their metabolites.

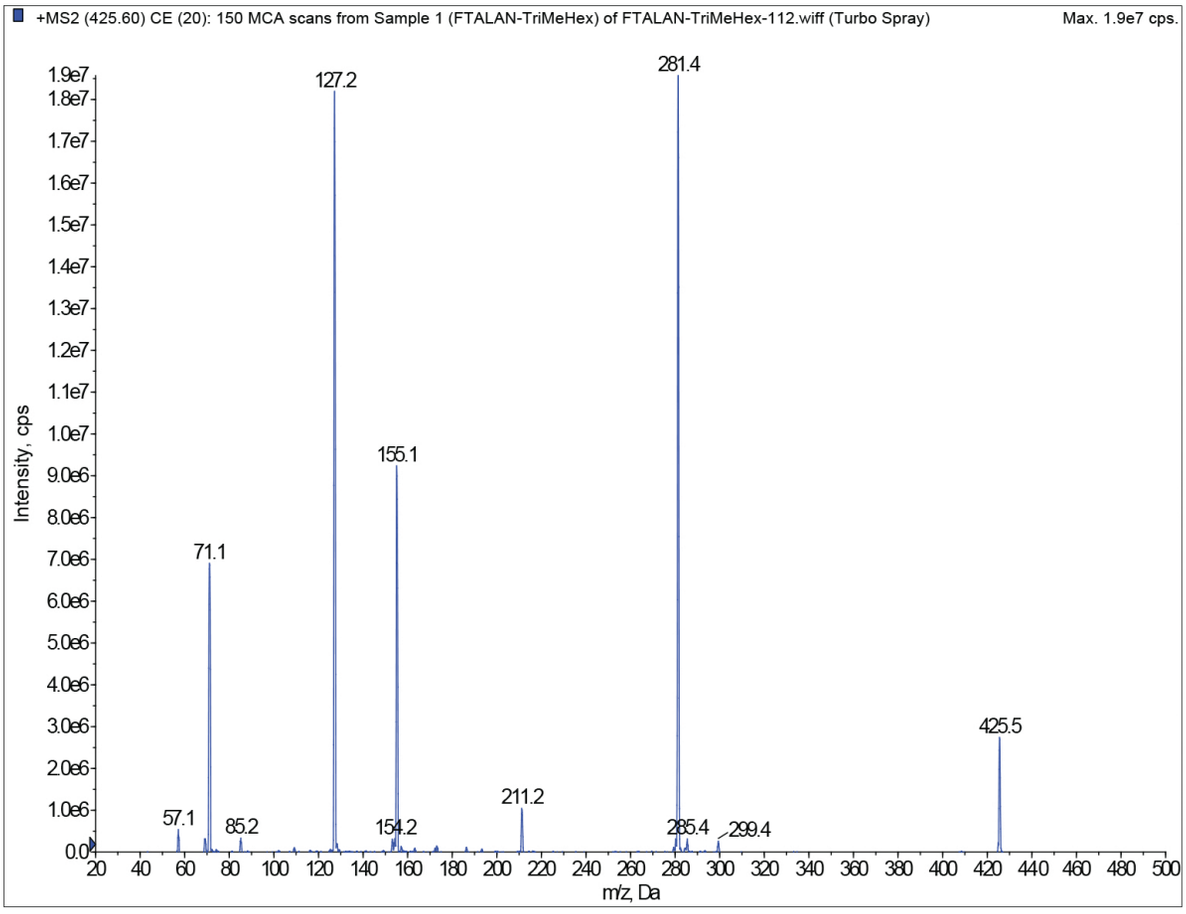


**Figure 3.** ESI mass spectrum of *cis* and *trans* isomers of di(3,5,5- trimethylhexyl)cyclohexane-1,2-dicarboxylate.

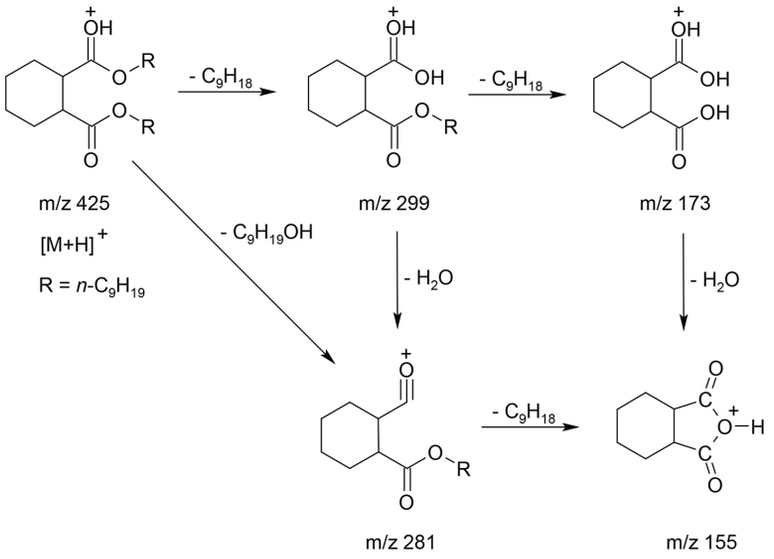


**Figure 4.** General mass fragmentation scheme of molecular ions $[M]^+$ of di(n- and isononyl)cyclohexane-1,2-dicarboxylates.

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## 3. Cross-linking agents

### 3.1. The branched poly(amines)

Epoxy resins due to their excellent mechanical and dielectric properties along with relatively low shrinkage, high resistance to elevated temperatures, and chemical media, but also the ease of processing are extensively applied in many fields, such as adhesives, coatings, and construction materials. This flexibility of properties of epoxy- derived materials is achieved due to the resins' tendency to undergo various modifications, usually by reactive and nonreactive fillers and different types of cross-linking agents [17, 18]. The curing of epoxy resins involves the formation of rigid three-dimensional network by reaction with cross-linking agents possessing usually more than two functional groups. High cross-linking density of epoxy systems is responsible for high impact strength of hardened epoxy resins and also at the same time for their inherent brittleness. Recently, lots of valuable papers have been published on modifications of epoxy resins, where incorporation of highly branched flexible modifiers considerably improved the mechanical behavior of epoxy materials [19–21]. Currently, hyperbranched polymers (HBPs) are of the biggest interest among all polymeric modifiers for epoxy resins. Branched structures of these resins are attractive due to their low viscosity and good ratio of reactive groups to molecular mass, especially when they are compared to their linear homologs. This makes HBPs perfect potential candidates as cross-linking agents for epoxy resins. Knowing the influence of branching and functionality of hyperbranched polymers on material's characteristics can be used to tailor its final properties [22, 23].

The hyperbranched poly(amines) may be used as specific additives as modifiers of the physicochemical properties of the epoxy resins. Especially, branched poly(amines) such as (N,N,N-tri(3-aminopropyl)amine and (N,N,N′,N′-tetra(3-aminopropyl) ethylene-diamines may be used as specific additives—cross-linking agents for this type of resins.

### 3.2. Synthesis of branched poly(amines)

Hyperbranched polymers can be prepared by various stepwise and repetitive chemical routes within which convergent and divergent methods are of the biggest practical meaning [24–26]. One of the easiest and the most effective way to synthesize the hyperbranched polyamines is cyanoethylation of primary amines followed by hydrogenation of resulting nitriles to generate primary amines. This process consists of an initial Michael's addition of a core amine to acrylonitrile, and then in the presence of Raney nickel hydrogenation to core amine, which can be further processed in a stepwise manner. Katriztky et al. [27] synthesized various nitriles with the addition of acetic acid as a catalyst with yields reaching 90% but then failed to obtain pure primary amines in hydrogenation process over Raney nickel catalyst with the addition of ammonia in methanol, preventing from formation of secondary amino functionality. Buhleier et al. [28] by means of $NaBH_4 \cdot CoCl_2$ reduced nitrile in 24% yield. After 15 years, this process was modified by using diisobutylaluminium hydride in a mixed solvent system of THF and hexane [29]. Worner and Mülhaupt performed hydrogenation of nitriles over Raney nickel in the presence of sodium hydroxide as a cocatalyst, which led to a decrease in reaction yield (ca. 70%) due to the retro-Michael reaction caused by the action of a strong base [30].

De Brabander-van der Berg and Meijer reported successful hydrogenation over Raney cobalt catalyst in water under $H_2$ pressure of 30–70 bar. Under these conditions no side products were obtained and 99.5% selectivity level per conversion was achieved [31].

The cross-linking agents (N,N,N-tri(3-aminopropyl)amine and (N,N,N′,N′-tetra(3-aminopropyl)ethylenediamines were obtained in the catalytic hydrogenation process of appropriate poly(nitriles) in the presence of modified silica support Ni catalyst.

Preparation of N,N,N-tricyanoethylamine (TCA) and N,N,N′,N′-tetracyanoethyl-1,2-ethylenediamine (TCED) was performed by means of bimolecular Michael addition of acrylonitrile to ammonia and ethylenediamine, respectively. The exotermic reaction of poly(nitriles) intermediates TCA and TCED starts with an addition of excessive acrylonitrile to the appropriate amine under ambient conditions.

The poly(nitriles) used for hydrogenation process were synthesized in the reaction of 30% water solution of ammonia or 1,2-ethylenediamine containing 1,4-dioxane and ionic liquid with an excessive amount of acrylonitrile. When the reaction was completed at 60°C, poly(nitriles) were separated by means of a separatory funnel and dried over magnesium sulfate in order to remove any traces of water.

The synthesized poly(nitriles) are the substrates in the hydrogenation reaction to obtain the primary poly(amines). This reaction was carried out in the presence of the Ni catalyst in the high-pressure autoclave giving the final product of the polyamines—(N,N,N-tri(3-aminopropyl)amine) (TAA) or (N,N,N′,N′-tetra(3-aminopropyl)-ethylenediamine)) (TAED) with 82.0% and 88.0% yields, respectively.

Poly(nitriles) used for hydrogenation reaction were obtained in a cyanoethylation process, as shown in **Figure 5** without purification procedures.

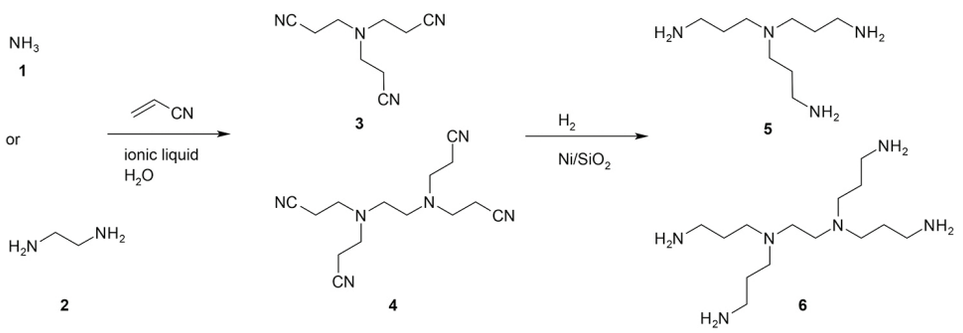


**Figure 5.** Cyanoethylation of ammonia and 1,2 ethylenediamine to N,N,N tricyanoethylamine (TCA) — 3 and N,N,N′,N′ tetracyanoethylo 1,2 ethylenediamine (TCED) 4 followed by their hydrogenation reaction gives (N,N,N tri(3 aminopropyl)amine) (TAA) — 5 and (N,N,N′,N′ tetra(3 aminopropyl)ethylenediamine)) (TAED) — 6, respectively.

The hydrogenation reactions were carried out at 135°C, under 10 bars for 6 h. In the case of TAA synthesis, yield of this reaction reached 85.7%, while for TAED exceeded 82%.

In case of hydrogenation of TCA for 0.14 mol of nitrile, 0.42 mol of $H_2$ is needed for total conversion of nitrile groups into primary amino groups. It was determined that to achieve full

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conversion of poly(nitriles) to the poly(amines) seven cycles of refilling hydrogen were necessary, which equaled to 0.42 mol of $H_2$. Exactly the same procedure was applied for hydrogenation of TCED, but full nitrile reduction was achieved after 12 cycles of hydrogen refill. In this case 0.72 mol of hydrogen was needed for the completion of the hydrogenation process (**Figure 6**).

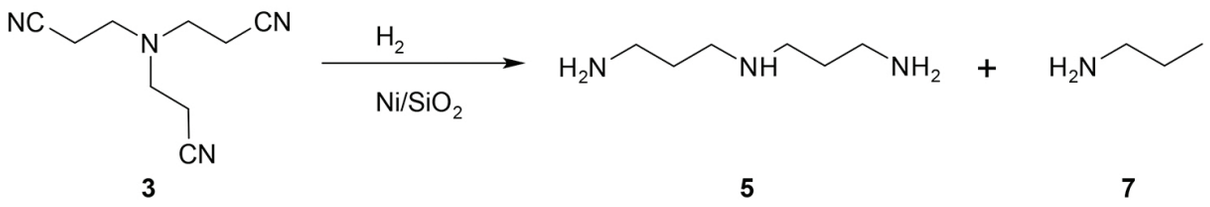


**Figure 6.** Hydrogenolysis of the TCA to N,N-diaminepropylamine and n-propylamine.

### 3.3. Identification of branched poly(amines)

In order to identify poly(amines) as the hydrogenation reaction products of the poly(nitriles), GC/MS, FTIR, and $^1$H NMR instrumental analytical techniques were used.

#### *3.3.1. GC/MS analysis*

GC/MS analyses of the branched polyamines were done by use of a gas chromatograph HP 6890 Series GC System (Hewlett-Packard) equipped with HP 5973 Network quadrupole mass selective spectrometric detector (Agilent Technologies) in a similar way as it was described in Section 2.3.1.

Hydrogenation process of TCED leads to the formation of N,N,N′-triaminepropyl-1,2-ethylenediamine with retention time $t_r$ =19.61 min and N,N,N′,N′-tetraaminepropyl-1,2-ethylenediamine (TAED) with $t_r$ = 23.60 min and small amounts of undesired by-products, which peaks are shown in **Figure 7**. In this reaction mixtures, besides the main products—components B and C, n-propylamine (component A) with $t_r$ =2.31 min is present. The mechanism of its formation probably is either by hydrogenolysis or retro-Michael reaction in which main products decomposes into molecules with lower molecular weights.

#### *3.3.2. FTIR analysis*

The standard Fourier Transform Infrared Spectrometer Nicolet 6700 type (FTIR) equipped with operating software Omnic from Thermo Company was used for the qualitative determination of the functional groups occurring in the hydrogenation reaction products. FTIR spectra were registered in the range of 4000–650 $cm^{-1}$ with the resolution of 4 $cm^{-1}$.

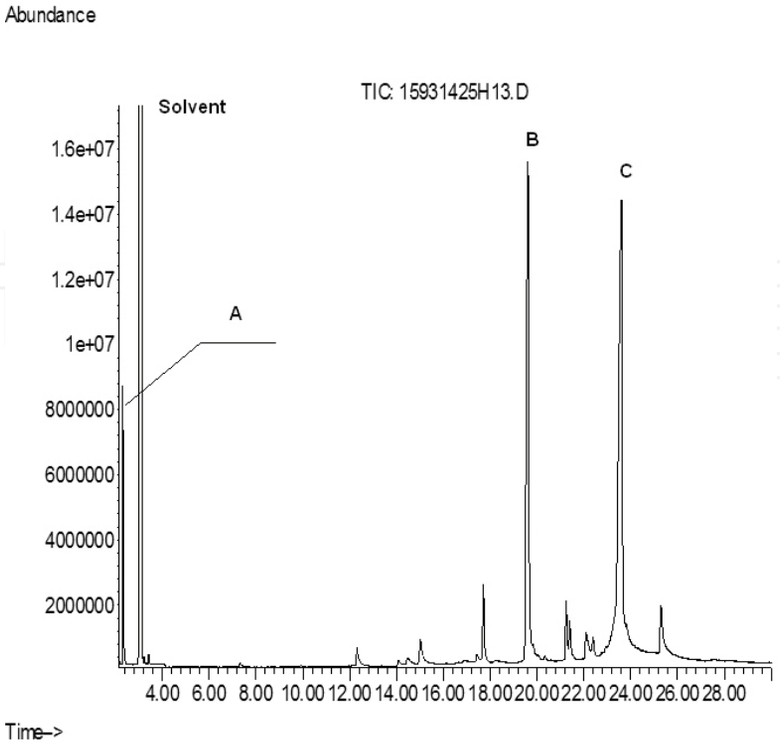


**Figure 7.** Chromatogram of the typical mixture of the hydrogenation products of N,N,N′,N′ tetracyanoethyl 1,2 ethylenediamine (TCED). GC peaks refer to: (A) n-propylamine; solvent — 1,4-dioxane; (B) N,N,N′ triaminepropyl-1,2-ethylenediamine; (C) N,N,N′,N′ tetraaminepropyl-1,2-ethylenediamine.

In the FTIR spectra (**Figure 8**) of the TCA and TCED there is apparent peak at 2250 $cm^{-1}$ assigned to C≡N group. In their FTIR spectra, after hydrogenation reaction of TCA and TCED nitriles in these groups almost completely disappeared, and instead broad peaks around 3350 $cm^{-1}$ assigned to N—H bonds in primary amino groups are observed.

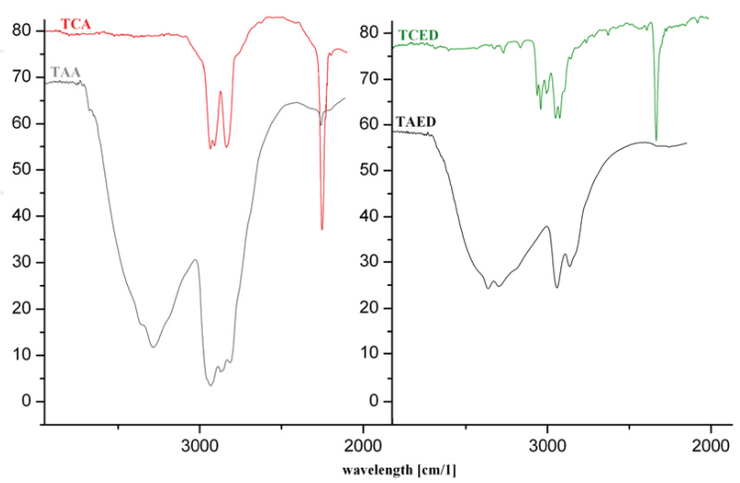


**Figure 8.** FTIR spectra of nitriles derived from ammonia (TCA) and ethylenediamine (TCED) and their hydrogenated products TAA and TAED.

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### *3.3.3. $^1H$ NMR analysis*

For $^1H$ NMR analyses the NMR Bruker Ultrashield was used. All spectra were taken at the frequency of 400 MHz, $CDCl_3$ with 0.03% TMS (v/v) was used as a solvent. Qualitative analyses were performed by using the Bruker Topspin 1 software.

The structures of final products after hydrogenation reactions were confirmed by use of $^1H$ NMR techniques. On the spectra recorded for TAA and TAED, there are shifts that could be assigned to protons corresponding to amine groups, meaning that the "core" molecules, ammonia and ethylenediamine, respectively, were successfully subjected to cyanoethylation reaction by acrylonitrile molecules.

The signals observed in the $^1H$ NMR spectra of TAA and TAED compounds (**Figure 9**) were taken to confirm their structures.

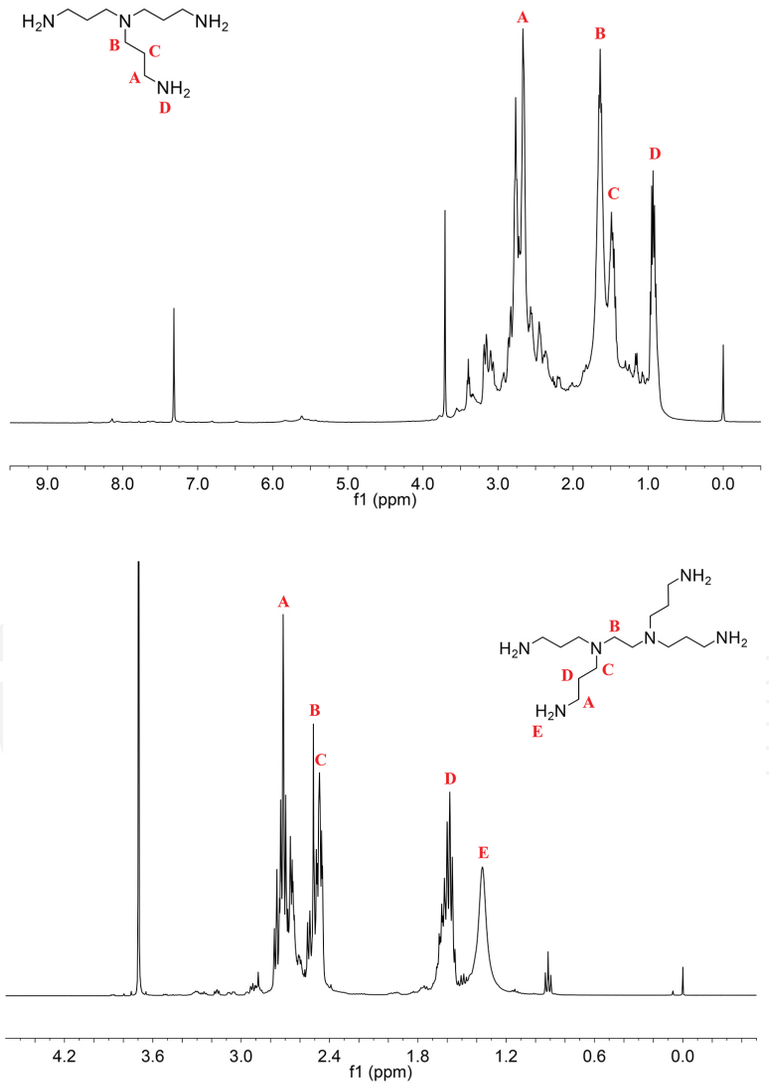


**Figure 9.** $^1H$ NMR ($CDCl_3$) spectra of TAA (above) and TAED (below).

In the case of TAA: 0.98 ppm, s, 6H, $–NH_2$; 1.50 ppm, p, $–CH_2–CH_2$; 1.70 ppm, t, 6H, $N–CH_2–CH_2$, 2.70 ppm, t, 6H, $–CH_2–NH_2$.

In the case of TAED**:** 1.36 ppm, s, 8H, $–NH_2$; 1.60 ppm, p, $–CH_2–CH_2$; 2.46 ppm, t, 8H, $N–CH_2–CH_2$, 2.50 ppm, s, 4H, $N–CH_2–CH_2–N$, 2.75 ppm, t, 8H, $–CH_2–NH_2$.

During hydrogenation process undesired reactions take place, leading to the formation of low-molecular weight products. After hydrogenation of poly(nitriles), besides the main products being TAA and TAED, the n-butylamine is one of the most abundant by- products present in the reaction mixture. It is formed by cleavage of bond between nitrogen heteroatom and β-carbon atom from acrylonitrile.

## 4. Conclusions

New generation additives for polymers such as plasticizers and cross-linking agents were synthesized in the catalytic hydrogenation process in the presence of Ni catalyst.

All hydrogenation products were analyzed using different analytical instrumental techniques such as GC/MS, ESI/MS, and spectroscopic techniques (e.g., $^1H$ NMR).

The new generation of plasticizers such as di(n- and isononyl)cyclohexane-1,2-dicarboxylates (DINCH components) are the new group of specific and safe plasticizers applied as the substitutes of di(alkyl) phthalates, especially di(2-ethylhexyl) phthalate (DEHP) and di(n- and isononyl) phthalates in polymers.

The identification of these compounds permits us to determine both the structures of the main products and their by-products as well. *Cis* and *trans* isomers of the cyclohexane-1,2-dicarboxylates may be applied to the identification of some DINCH constituents extracted from polymers and also in the elucidation of their structures in the human metabolites. ESI/MS mode analysis of these compounds and the knowledge about their mass fragmentation enable their detection, although without differentiation between individual *cis* and *trans* isomers. The obtained identification results concerning the determination of the individual chemical structures of some *cis* and *trans* di(n- and isoalkyl($C_4–C_9$))cyclohexane-1,2-dicarboxylates isomers (DINCH) maybe used in their determination of exposure and risk assessments.

Also, poly(amines) possessing usually more than two functional groups are very useful as cross-linking agents and are used in the modification of physicochemical properties of the epoxy resins by the most effective chemicals.

The obtained results from the analysis of the final product of hydrogenation reaction of both *cis* and *trans* di(n- and isoalkyl($C_4–C_9$))cyclohexane-1,2-dicarboxylates isomers (DINCH) and branched poly(amines) are useful in the optimization of processes of their production in an industrial scale.

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