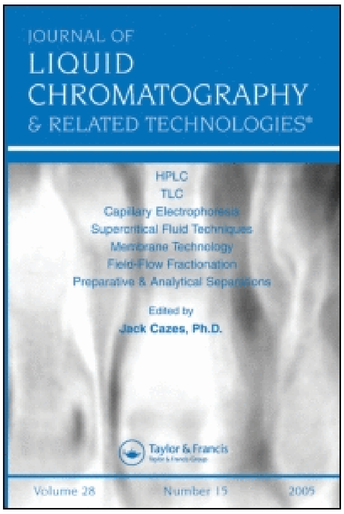

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Determination of Residues of 1,4,7-Trioxacyclotridecane-8,13-Dione in Polyester Polymers by Liquid Chromatography

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Abstract: A new method is proposed for determination of the residue of 1,4,7-trioxacyclotridecane-8-13-dione in the polyester polymer used for production of elastic polyurethane foams, which in turn are widely used in car industry. This compound is responsible, among other factors, for the phenomenon of fogging up of internal car windows. The method is based on extraction of the residue from the polyester, followed by HPLC analysis with a refractive index detector. In the paper, the procedures of isolation, identification, and purification of the compound are described. Some results are given of determination of 1,4,7-trioxacyclotridecane-8-13-dione in samples of polyester with different contents of the analyte. The proposed method is characterised by high precision, permitting the determination of 0.025% of the compound residue in the polymer.

Keywords: 1,4,7-Trioxacyclotridecane-8-13-dione, Polyurethane foams, Fogging up, HPLC

INTRODUCTION

Different plastic materials constitute about 10% of a mass of a car, and average contribution of plastics in the total mass of a car increases. The majority of plastics is used for production of car interiors and accessories.[1] Polyvinyl chloride (PVC) and polyurethane foams are basic components of

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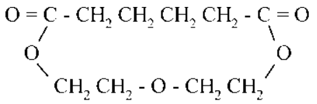
high molecular polymers used for production of car upholstery, floor mats, ceiling lining, or sound proofing, etc. Elastic polyurethane foams are characterized by good mechanical and thermal stability. However, these compounds contain some unwanted compounds responsible for fogging,[2] emitting volatile organic compounds of unpleasant odors, and internally condensing on car windows. The condensate, apart from toxic effects, also restricts driver's visibility. The main chemical compound responsible for such condensation is 8,13-dioxo-1,4,7-trioxacyclotridecane,[3,4] also known as lactone.



8,13-dioxo-1,4,7-trioxacyclotridecane (lactone)

Conventional polyesters do not meet the requirements of the modern car industry. Thus, new technologies are being searched for production of polyurethane foams of diminished contents of lactone. Controlling the level of the "fogging" compounds becomes a must. Such controlling may be achieved by determining the level of the "fogging" effect, or by determining the amount of the lactone in the polyester. The second option looks better, as it permits a determination of the lactone level at the earlier stages of the production of the polyurethane foam.

The aim of this paper was to propose a method for lactone determination in polyesters. The method is based on liquid chromatography. Since the lactone molecule does not contain chromophore groups, use of UV Vis detectors is useless. In the proposed method, a differential refractometer detector is used, to measure differences of refraction indices of the eluent and the compounds studied.

EXPERIMENTAL

Chemicals and Reagents

Methanol was HPLC grade, supplied by Merck (Germany). Adipic acid, diethylene glycol, ethyl acetate, hexane, and ethanol were analytical grade by POCh (Poland). Aluminiumoxid 90 active neutral, silica gel 60 extra pure for column chromatography, and dibutyltin dilaurate for synthesis, came from Merck (Germany). Ultrapure water was prepared using a Milli-Q filter system Millipore (USA).

The standard solution of lactone −20 mg/mL was prepared by carefully weighting 100 mg of lactone and dissolving in 5 mL of ethanol.

The series of standard curves were prepared, with concentration ranging from 0.05 to 1 mg/mL. The dependency of the concentration and the peak height was calculated by the use of linear regression analysis.

Equipment

We used a liquid chromatograph HP-1050 (Hewlett-Packard) equipped with a refractometric detector (Waters), Rheodyne dosing valve 7025 with a sample loop of 25 μL capacity, LiChrospher 100 RP-18 5 μm column, 4.6 × 250 mm Merck (Germany), and gas chromatograph HP 5890 made by Hewlett-Packard with a DB-1 column of 30 m × 0.53 mm (J&W Scientific).

Obtaining and Identification of 8,13-Dioxo-1,4,7-trioxacyclotridecane

The synthesis of lactone was performed on the basis of the method of depolymerisation developed by Carothers,[5] later used by Dale,[6] and adapted by Binns and Taylor[3] for obtaining the lactone.

The synthesis involves the following stages:

Polymerisation of adipic acid and diethylene glycol at high temperature,
Removal of unreacted substrates,
Catalytic depolymerisation by dibutyltin dilaurate with continuous product removal.

Adipic acid, 0.1 mole, (14.75 g) and 0.1 mole of diethylene glycol (10.91 g) were heated in a 50 mL flask under reflux, for 3 h at 190°C. The contents of the flask was subjected to distillation under reduced pressure (4 mm Hg) at 190°C for 3 h. At the next step, 0.5 g of dibutyltin dilaurate was added to the flask, and the contents was distilled under reduced pressure (4 mm Hg) to get pale yellow crystals and subjected to redistillation under reduced pressure (4 mm Hg) at 200°C.

The product was dissolved in ethyl acetate and passed through a column filled with neutral Al_2O_3 in order to remove the polymer. After evaporation of the solvent, the crystals were dissolved in a mixture of ethyl acetate and hexane at 1:3, and injected onto the column with SiO_2. Elution was performed with the above described mixture, and during this process particular fractions were collected. The fractions were tested for the presence of lactone by the use of HPLC. The procedure of the standard purification was repeated till pure lactone was obtained.

The crystals obtained were identified by determining the melting point, elemental analysis, by NMR study (Fig. 1). Finally, the purity of the product was estimated by gas chromatography. The compound obtained was characterized by the following parameters:

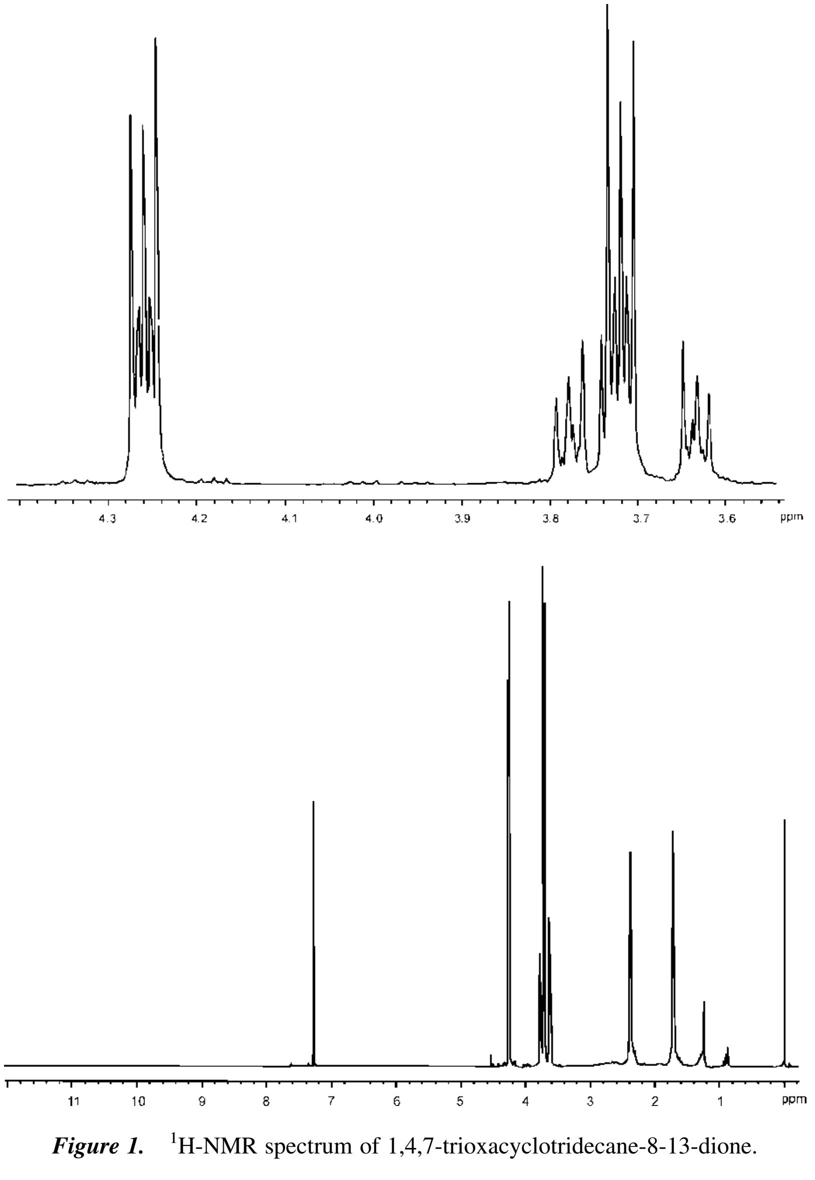


Figure 1. ^{1}H-NMR spectrum of 1,4,7-trioxacyclotridecane-8-13-dione.

Melting point: 79–80°C,

Elemental analysis: calculated for $C_{10}H_{16}O_5$–C 0.555, H 0.074, O 0.370; determined – C 0.556, H 0,074,

^{1}H-NMR analysis ($CDCl_3$)–δ 1.71–1.75 (m, 4H, CH_2); δ 2.37–2.40 (m, 4H, $OCOCH_2$); δ 3.70–3.74 (dt, 4H, OCH_2); δ 4.24–4.28 (m, 4H, OCH_2).

Figure 2 presents a gas chromatogram of an ethanol solution of lactone standard. One should note the peaks assigned to ethanol and the separate peak assigned to lactone, the latter characterised by the retention time of 10.1 min. The analysis was made on a gas chromatograph HP 5890, using a DB-1 column, with temperature programmed in the range from 150 to 250°C increasing by 10°C/min.

The obtained NMR results unambiguously prove that the product of the synthesis performed is composed of 8,13-dioxo-1,4,7-trioxacyclotridecane. The results of the gas chromatographic analysis (normalization to 100%) and NMR spectrum of the lactone obtained testify to the high purity of the pattern (99.8%).

Emission of Lactone from the Polyester

A portion of 2 ± 0.01 g of commercial polyester PE-1 was placed in a 100 ML Erlenmeyer flask of 100 mL, to which 25 mL of ethanol was added. The flask was strongly shaken till its contents were fully homogenised. Then, it was placed in a 100 mL centrifugal cell and subjected to centrifuging at the rate

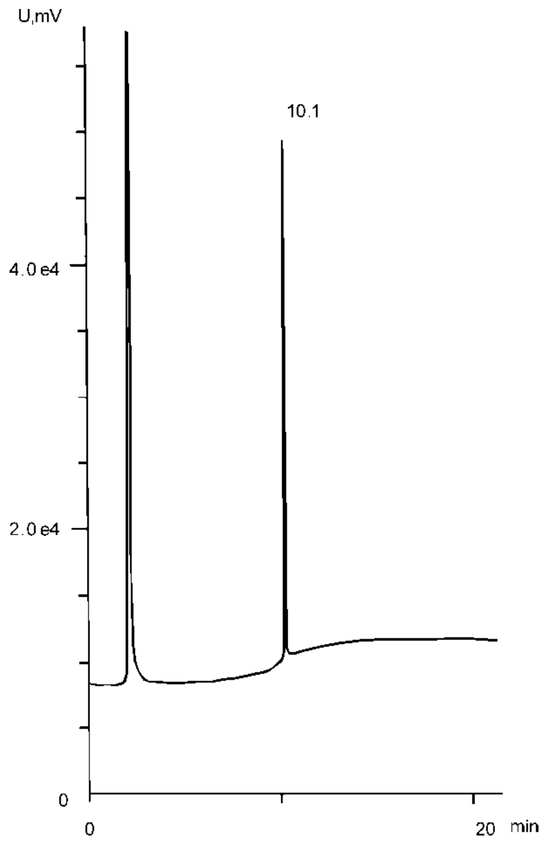


Figure 2. GC chromatogram of lactone standard.

3000 rev/min for 10 min. After centrifuging, the transparent upper alcohol layer was subjected to chromatographic analysis.

RESULTS AND DISCUSSION

Optimization of Chromatographic Analysis

The chromatographic conditions were determined by the choice of a proper stationary phase and mobile phase. The properties of lactone and polyester limited the choice of possible phases. A few standard column packings were tested for this purpose, and the RP-18 column was finally used. The optimum mobile phase had to dissolve the extract obtained, thus, permitting complete separation of lactone and the components migrating from polyester to ethanol in a shortest possible time. The mobile phase parameters were established on the basis of the retention characteristics of the lactone and extracts pattern of the samples. Finally, the mobile phase was composed of methanol and water at the proportions, 30/70% vol.

Repeatability

Repeatability of the chromatographic system was tested by the injection of a pattern solution containing 0.2 mg/mL analyte ($n = 8$). Repeatability of the retention time and peak height for lactone was: 12.95 ± 0.03 min; RSD = 0.125%, and 11.22 ± 0.15 mm; RSD = 1.15%, respectively. Even if the samples were injected manually, the obtained results, including RSD values, were quite repeatable and, thus, of good quality.

Optimisation of the Process of Extraction and Analytical Procedures

After optimization of the chromatographic conditions, the suitability of HPLC for lactone determination was tested. Several of the lactone standard solutions in ethanol were prepared with the following concentrations: 0.05, 0.1, 0.2, 0.5, and 1.0 mg/mL. They were injected onto the column and their chromatograms were recorded. The peaks assigned to lactone were sharp, symmetric, and fully resolved. On the basis of the chromatograms, a calibration curve was drawn showing the relation between the height of lactone peaks and the lactone concentrations. In the concentration range studied, the calibration curve could be approximated by a line $y = ax + b$, where $a = 129$ and $b = -2.3$, and the linear regression coefficient was $r = 0.998$. The results of the test prove that the method of liquid chromatography can be used for lactone determination in polyesters.

Limits of Detection and Quantification

The limit of detection (LOD) was determined to be 10 μg/mL, as defined by the concentration of analyte giving a signal to noise ratio of 3 : 1. The limit of quantification (LOQ) was 50 μg/mL, as defined by the lowest concentration of the analyte that can be detected by the use of the described method.

Recovery Determination

At the next stage of our research, the level of extraction of the lactone from the polyester was determined. For this purpose, six determinations were made for pairs of samples containing the same amounts of the polyester. Each time an amount of the lactone pattern was added to a sample of each pair. Each pair of samples were analyzed by the above described procedure based on the obtained results; the recovery rate of the compound was determined, varying in the range 60–70%. For such recovery rates, the quantitative analysis could not be performed on the basis of the calibration curve. The obtained results were significantly underestimated, and an introduction of a correction coefficient provoked a significant error in the determination. Therefore, the analytical method of standard addition, often used in analysis of complex matrices, was chosen. In this method, the determination is independent of the recovery rate, as the extraction of the component under determination and the pattern is performed to the same extent. The determination is made for the sample studied and for the sample with the known amount of the pattern. The pattern and the sample are determined in the same conditions. Even if the character or amount of polluting substances is unknown, it can be assumed that the influence of these substances affects the measurement in the same way for both determinations.

Determination of Lactone in Polyesters

The content of lactone was determined in two commercially available polyesters labeled as PE-1 and PE-2. The results of the quantitative analysis and

Table 1. Analysis of two conventional polyesters (n = 8)

Polyester	Confidence interval[a] (%)	RSD[b] (%)
PE-1	1.25 ± 0.03	2.60
PE-2	1.16 ± 0.02	2.16

[a] The interval containing the real value with the probability of 95%.

[b] Relative standard deviation characterising the precision of the method.

Table 2. Analysis of three weak-fogging polyesters (n = 8)

Polyester	Confidence interval[a] (%)	RSD[b] (%)
PE-3	0.23 ± 0.012	5.38
PE-4	0.24 ± 0.02	4.56
PE-5[c]	≅ 0.016	>0.05

[a]and [b]as in Table 1.

[c]Due to small content of lactone, the standard was added in 4 mg.

statistical data are given in Table 1. Table 2 presents the analogous data on three weak fogging polyesters labeled as PE-3, PE-4, and PE-5.

Figure 3 presents the example chromatograms of (a) the sample studied, (b) the same sample with the standard added, obtained on determination of lactone in the polyester PE-1, and (c) the chromatogram of the standard dissolved in ethanol in a concentration of 1 mg/mL. Under the chromatographic conditions applied, the lactone retention time was 13 min. The peaks assigned to lactone were sharp and symmetric, so they were suitable

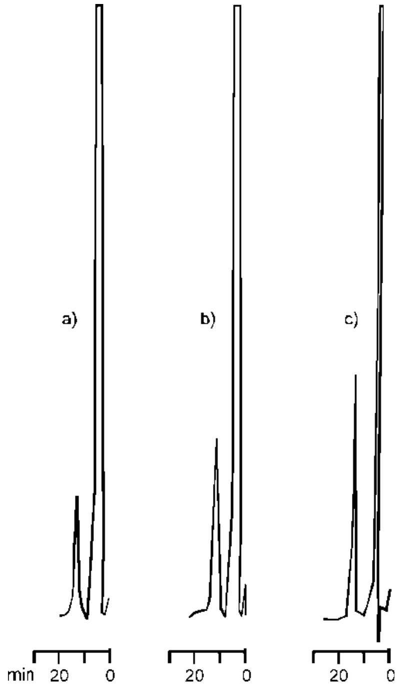


Figure 3. LC chromatograms of a) polyester PE-1 extract, b) polyester PE-1 extract with lactone in the amount of 5 mg per 1 g of the polyester, c) lactone standard 1 mg/mL.

for interpretation in quantitative analysis. The peaks assigned to ethanol appeared in the dead time. The chromatograms (a) and (b) show characteristic tails of the peaks, indicating that ethanol was eluted together with the unreacted polyethylene glycol and impurities.

CONCLUSIONS

The tests performed have confirmed the suitability of the method proposed for determination of lactone in polyesters. The method is characterized by a fast and easy way of sample preparation (the sample studied and the sample with a standard). As indicated by the data presented in Tables 1 and 2, the method is characterized by high precision. Detection limit is equal to 0.1 mg of lactone in 1 mL of ethanol. According to the above described procedure, the percentage detection limit in polymer is equal to a concentration level of 0.025%.

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