



# Combined size exclusion chromatography, supercritical fluid chromatography and electrospray ionization mass spectrometry for the analysis of complex aliphatic polyesters



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## ABSTRACT

Aliphatic polyesters are complex products of polycondensation that are distributed regarding the degree of polycondensation, the end group functionality and the molecular topology. To address the molecular heterogeneity of polyesters based on phthalic acid and propylene glycol, for the first time the combination of SEC, SFC and ESI-MS have been used. In a first set of experiments, samples were fractionated by SEC and the collected fractions analyzed by SFC for a tentative assignment of the degrees of polycondensation. More conclusive results were obtained by semi-preparative SFC fractionation of the bulk samples and the subsequent analysis of the collected fractions by ESI-MS. The ESI-MS spectra of the SFC fractions provided detailed information on the presence of linear and cyclic oligomers, their degrees of polycondensation and their end groups. Information on the presence of propylene oxide oligomers was also obtained and it was shown how they were inserted in the polymer structures. Compared to previous work, the present approach provides significantly more detailed information on the molecular complexity of aliphatic polyesters. This is mainly due to the fact that SFC has been used as the second chromatographic dimension which is known to have superior separation capabilities.

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## 1. Introduction

Complex polymers are distributed in molecular parameters such as molar mass, chemical composition, end group functionality and topology [1]. These parameters determine the properties of the final materials and eventually their use in technical applications. Polyester resins are important industrial products due to their cost effectiveness, the easy processing and mixing capacity with reinforcements, fast curing with trace amounts of volatile products, great dimensional stability and availability of a variety of grades. The physical and mechanical properties of polyesters are brought about by various combinations of unsaturated and saturated diacids with glycolic compounds. Their molar ratios determine the composition of the end products which, essentially, are mixtures of prepolymers differing in molar mass, chemical composition, the degree of branching, and end group functionality.

Although the synthesis, curing behavior and properties of numerous types of aliphatic polyester resins have been addressed extensively, so far analysis has mainly focused on bulk parameters [2–4]. Phthalic anhydride (PA) is an important component in the production of aliphatic polyester resins that are used for

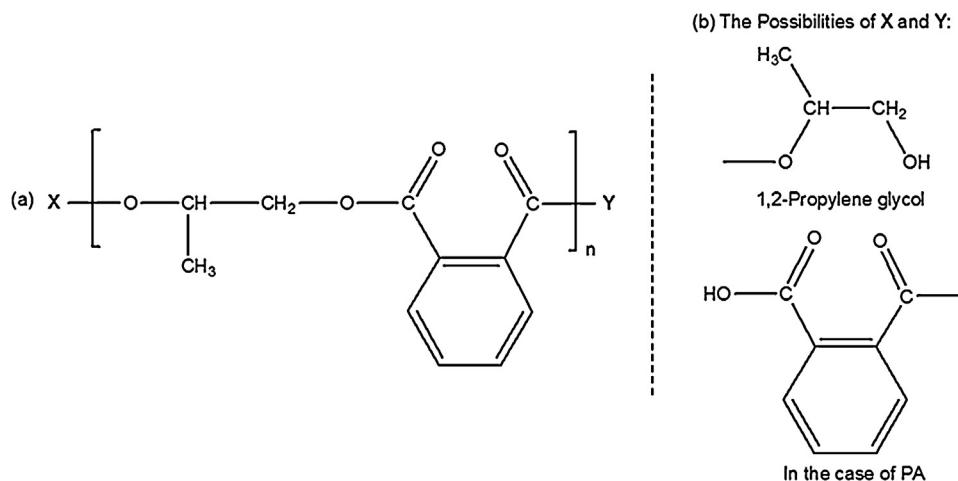
example in the coatings industry. The polycondensation mechanism and the kinetics of PA, maleic anhydride and 1,2-propylene glycol have been extensively investigated [5–7]. In all instances, the main esterification reaction with regards to the occurrence of isomerization, double bond saturation and transesterification as side reactions was in the focus of the investigations. By now it is generally accepted that the end result of the polymerization is a material with an extremely complex chemical composition; and since this heterogeneity influences polymer properties, it is important to have methods or techniques available to determine these characteristics.

Traditional analytical methods such as polarography [8–10], infrared spectroscopy [11,12], and bromine number determination [13] have been used. <sup>1</sup>H and <sup>13</sup>C NMR analysis in combination with physical properties [14], modeling simulations [15,16] as well as SEC [5,17] proved to be suitable for understanding the polyesterification mechanism, the side reactions involved and the related properties [18,19]. Mass spectrometry (MS) has been used to investigate chemical compositions [20], the presence of cyclic oligomers [21] as well as to assist in-depth studies regarding reaction mechanisms, kinetics and degradation [22–24]. SEC (with a variety of detectors) has been the core method for the analysis of molar mass distributions [25–27].

In a very recent publication of some of the present authors the combination of SEC and MALDI-TOF MS was used to elucidate the

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**Fig. 1.** Proposed polyester structure where (a) refers to the repeating unit of polyesters PA–PG and (b) to the different possible end group combinations.

molecular complexity of phthalic anhydride-1,2-propylene glycol polyesters which serve as building blocks for the more complex industrial aliphatic resin variety [28]. The goal was to investigate samples that were removed at varying stages of the polyesterification reaction. SEC was employed to follow the course of the polycondensation reaction and compare the evolution of molar masses. Subsequent off-line coupling with MALDI–TOF MS served as a detection as well as core method to determine the chemical composition and to identify functional end groups. For the purpose of the investigations model polyesters of phthalic anhydride with 1,2-propylene glycol (PA–PG) were synthesized where the glycol was added in 30% molar excess relative to the anhydride. The proposed structures having differences in end group functionalities are given in Fig. 1.

The investigations showed that detailed information on end group functionalities as a function of molar mass could be obtained. However, as SEC separation according to hydrodynamic volume intrinsically has a rather low resolution compared to HPLC methods that make use of specific interactions between the analyte and the stationary phase, it was the aim of further studies to use fractionation methods with superior selectivity.

Supercritical fluid chromatography (SFC) has, since its first application to polymer analysis in 1970 [29], been shown to offer several advantages compared to HPLC for the separation of polymeric materials [30,37]. Benefits of SFC include improved chromatographic performance due to the advantageous properties of the supercritical mobile phase, a reduction in the consumption of toxic solvents, and inherent amenability to (semi-)preparative isolation of separated compounds. While open tubular capillary SFC has been utilized with notable success for polymer analysis [31], the packed-column format has largely supplanted capillary SFC in the last 20 years [32,33]. The recent commercial availability of a new generation of SFC instruments designed to exploit the benefits of sub-2  $\mu\text{m}$  particle-packed columns under SFC conditions has further extended the applicability of packed-column SFC to fast, efficient analyses [34].

Now, for the first time we report on the analysis of aliphatic polyesters by the combination of SEC, SFC and ESI–MS. The experimental protocol was as follows: in a first step, preparative SEC fractionations were conducted, the fractions collected and subjected to SFC for the analysis of the degree of polymerization. In a second step the samples were subjected to preparative SFC, the fractions collected and analysed by ESI–MS for the analysis of the oligomer composition. Using this multidimensional approach, very detailed information on the molecular composition of aliphatic polyesters was obtained. The advantage of using SFC as the second

chromatographic dimension after SEC is that (1) SFC has superior separation capabilities and (2) only very low amounts of sample fractions are required.

## 2. Experimental

### 2.1. Size exclusion chromatography

Separations were achieved on an Agilent 1260 Infinity series instrument consisting of a 1260 degasser and quaternary pump, 1260 ALS auto-sampler, a 1260 variable wavelength UV detector operating at a wavelength of 254 nm and a PL-ELS 1200 series evaporative light scattering detector (Chemetrix (Pty) Limited South Africa, Agilent Technologies). The stationary phases used were a set of three columns, PLgel 3  $\mu\text{m}$  Guard (50  $\times$  7.5 mm) and 2 PLgel 3  $\mu\text{m}$  Mixed-E (300  $\times$  7.5 mm) (Chemetrix (Pty) Limited South Africa, Agilent Technologies). A flow rate of 1 mL/min was applied with a column oven temperature of 30°C. The injection volume was 20  $\mu\text{L}$ , with a sample concentration of 5 mg/mL in tetrahydrofuran (THF), HPLC-grade (Sigma–Aldrich, South Africa). Data collection was done by the “PSS WinGPC Unity” (Polymer Standards Service, Germany) software. All narrowly distributed polymer standards of polystyrene (PS) were purchased from Chemetrix (Pty) Limited South Africa, Agilent Technologies.

From SEC, the eluting oligomer-separated peaks of the last sample in the kinetic series, s28 (see Table 1), was repetitively fractionated. A total of 20 SEC fractionations of the sample at 25 mg/mL were conducted to ensure enough sample material per fraction for SFC analysis. In order to follow the elution time of each of the fractions, a UV detector at 254 nm wavelength was employed. After the evaporation of the mobile phase, the concentrated fractions were re-dissolved in 1.5 mL acetonitrile (ACN) (MS grade, Sigma–Aldrich, South Africa).

### 2.2. Supercritical fluid chromatography

SFC analyses were performed on an Acquity UPC<sup>2</sup> system equipped with a binary solvent delivery pump (maximum pressure 400 bar), autosampler, column oven compartment (including two 6-port column selection valves), photodiode array (PDA) detector and Acquity ELS detector and controlled by Empower software (Waters, Milford, MA, USA). UV data were recorded between 210 and 400 nm at an acquisition rate of 20 Hz (UV chromatograms at 254 nm are presented herein). The ELSD was connected between the PDA detector and the back-pressure regulator (BPR) using an ELS splitter kit (Waters). ELSD parameters were as follows:

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