



Analysis of complex phthalic acid based polyesters by the combination of size exclusion chromatography and matrix-assisted laser desorption/ionization mass spectrometry



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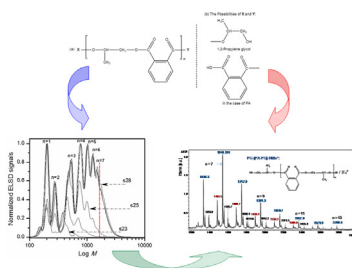
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HIGHLIGHTS

- Complex aliphatic polyesters have been prepared in kinetic runs.
- Kinetic samples have been analysed by SEC and the molar mass distributions determined.
- SEC indicates complex composition of the samples.
- Single oligomers were fractionated and analysed by MALDI-TOF, oligomer masses were used to obtain oligomer calibration for SEC.
- Complex functionality type distributions of the kinetic samples and the fractionated oligomers were analysed.

GRAPHICAL ABSTRACT



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ABSTRACT

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) was used in conjunction with size exclusion chromatography (SEC) to investigate a model polyester system based on phthalic anhydride–1,2-propylene glycol. The polyesters were synthesized with a 30% molar excess of glycol, with kinetic samples being removed during different intervals of the polyesterification reaction. SEC was used to track the course of the reaction by determining the molecular weight and molecular weight distributions before subsequent off-line coupling with MALDI-TOF MS as a selective detection method to determine the chemical composition, identify the functionality type distributions as well as assist in assigning structural conformations. Mass spectrometry analysis proved to be a highly effective tool to facilitate the identification of the narrowly dispersed fractions obtained from the chromatographic separations as well as serve as a core method to investigate the heterogeneous nature of the bulk kinetic samples. Through the hyphenation of these sophisticated polymer characterization techniques, information on the molecular heterogeneity of the model polyesters, showing a complex variety of possible distributions, was obtained.

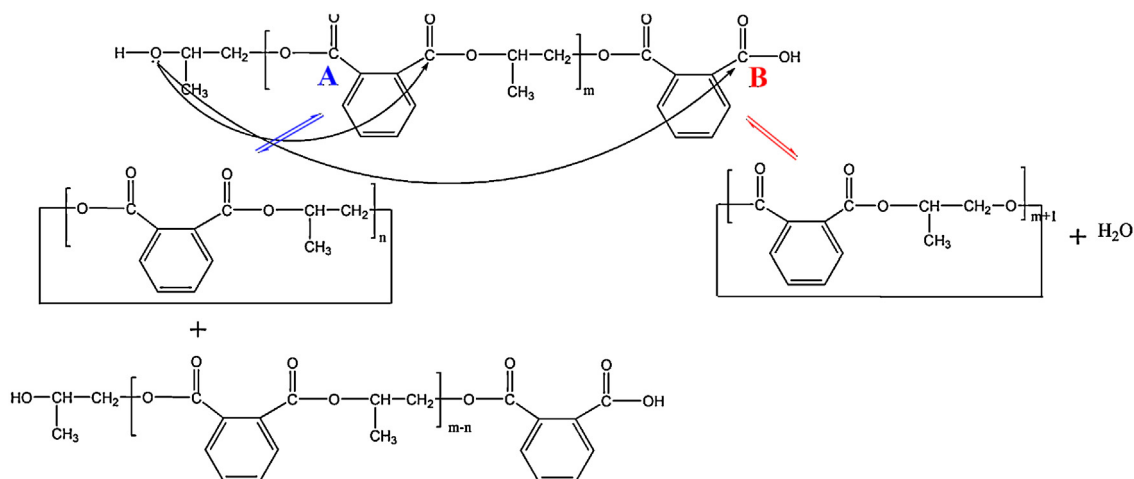
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1. Introduction

Polyester resins are known to have widespread use in industry due to their cost efficiency, processing and mixing ability with reinforcements, fast curing with low levels of volatile products, great

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Scheme 1. Formation of cyclic structures via intra-molecular transesterification reactions (A) back-biting and chain end-end reactions (B).

dimensional stability and large range of grades available. The basis for their extensive industrial application are the different physical and mechanical properties brought about by the implementation of various combinations of unsaturated and saturated diacids with glycolic compounds and their molar ratios that provide products with a large variety of final applications. Essentially, these resins are mixtures of prepolymers differing in molecular weight, chemical composition, the degree of branching, endgroup functionality and structural conformations. An extensive number of studies have been reported on the synthesis, characterization, curing behaviour and properties of numerous types of aliphatic polyester resins [1–3]. As the saturated constituent, phthalic anhydride (PA) in particular, plays an important role in the production of aliphatic polyester resins implemented for example in the coatings industry. Several studies have discussed this particular anhydride system in combination with other diacids and diols. The related polycondensation mechanism and kinetics in combination with maleic anhydride and 1,2-propylene glycol have been extensively investigated and well documented [4–6]. In all instances, the focus was on the main esterification reaction with regards to the occurrence of isomerization, double bond saturation and transesterification as side reactions. Due to the fact that most of the aliphatic resin applications involve dilution with one or several vinyl monomers capable of free radical copolymerization, the incorporation of an unsaturated anhydride and/or dicarboxylic acid such as maleic anhydride is essential to provide the unsaturated bonds on the polymer chains. These are to be cross-linked in the presence of free-radical initiators to yield the desired thermosets [7,8]. Consequently, information on the transesterification side reactions stemming from the saturated diacid tends not to address isomerization and double bond saturation. Transesterification reactions participate equally in producing differences in chemical composition by alcoholysis, acidolysis and ester–ester interchange as well as the formation of cyclic products by intra-molecular and/or intermolecular reactions of the OH and COOH groups via back-biting and chain-end reactions, see Scheme 1 [9,10].

These ester interchanges within the same or different compounds, would redistribute molecular weight and functional endgroups of the polyester molecules, resulting in a statistical distribution of macromolecular units and chain ends [11,12]. The end result is a system 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.

Classical analytical and physicochemical values derived from techniques such as the hydroxyl and acid number determination are often unable to describe molecular weight distributions, follow the course of polycondensation, distinguish differences between individual samples, explain the differences in their properties and the relationship between the composition of the starting resins and properties of the cross-linked materials based on them [13]. Structural characterization has been conducted using polarography [14–16], infrared spectroscopy [17,18], ebullioscopy [14] and bromine number determination [19]. ^1H and ^{13}C NMR analysis in combination with physical properties [20], modelling simulations [21,22] as well as SEC [4,23] proved to be well established methods of understanding the polyesterification mechanism, the side reactions involved and their related properties [24,25].

Due to the complex molecular and chemical nature of polyester resins, characterization by means of advanced liquid chromatography has, however, been less frequent. SEC is known to be the most commonly applied LC technique for separation based on the hydrodynamic volume (“effective” molecular size) of molecules in solution and the extent to which they are excluded from the porous particles of the stationary phase. In essence, it has completely replaced previous tedious fractionation methods used for the determination of the molecular weight and the molecular weight distribution of synthetic macromolecules [26,27].

SEC has however intrinsic limitations in that it cannot distinguish between heterogeneities in composition, chain architecture, microstructure and functionality. In order to address this problem several selective detection techniques have been combined with SEC. Hyphenated techniques involving SEC have been covered extensively in literature [28–30]. Podzimek et al. [13,31] specifically summarized the application and suitability of SEC for the analysis of synthetic resins. The analysis of several commercial epoxy resin and polyester resin samples was demonstrated via the use of SEC-MALLS and reversed phase HPLC. The results clearly showed the challenges involved to separate the molecules according to molecular weight, molecular weight distribution, functionality type and functionality type distribution. Other LC studies combining SEC and HPLC for a variety of polyesters have also been published [24,31,32].

Over the past two decades the application of mass spectrometry for polymer characterization has experienced tremendous growth due to its versatility, relative ease of operation and the wealth of information that can be acquired in the process [33–35]. Specifically for MALDI-TOF MS numerous examples exist in the literature

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