

In-depth study of the synthesis of polyamides in the melt using biacetal derivatives of galactaric acid



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ABSTRACT

In recent years, the incorporation of sugar-derived, cyclic moieties into polymer structures is gaining the interest of researchers and industry. Factors like the general availability of carbohydrate sources and the unique properties of polymers therefrom contribute to their popularity, but on the other hand the presence of additional functional groups e.g. cyclic acetal, might lead to side reactions. The aim of this study is to investigate the different processes occurring during polymerization of 2,3:4,5-di-*O*-isopropylidene-galactarate (GalXMe) and 2,3:4,5-di-*O*-methylene-galactarate derivatives (GalXH). The substrates and the polymers obtained by means of the melt polycondensation of ester functionalized monomers and polyamide salts are analyzed by combined TGA, GPC, NMR, LC-MS and Maldi-ToF techniques. Furthermore, melt polymerization of polyamide salts was followed by TGA-MS, which allowed identifying degradation products produced during the polymerization.

1. Introduction

During the last decades carbohydrate-derived polymers have received a lot of attention mostly on account of the widespread availability of the sources from which the monomers can be produced. The chemicals which can be obtained by extraction and chemical modification of biomass offer a wide variety of structures: from simple adipic acid to bicyclic structures of isosorbide [1–4]. By these techniques it is now possible to obtain diols, diamines, dicarboxylic acids or esters from different renewable sources. All these monomers can be used for the synthesis of polymers [4–6]. Biacetalized derivatives of galactaric acid (also known as mucic acid) are produced by chemical modification of galacturonic acid extracted from beet root pulp, a waste product from sugar production (Fig. 1). This type of monomers have already been investigated as promising substrates for polyesters [5,7–13], polyamides [12,14–18] and polyurethanes [19,20].

These unique cyclic moieties are known to enhance the thermal properties of polymers [10]; however the presence of oxygen linkages may hamper the thermal stability of the biacetal moieties during or after polymerization, and therefore lead to the occurrence of side reactions, manifested in discoloration, crosslinking or degradation of the material [21]. This phenomenon is particularly disturbing during high temperature polycondensation required for the synthesis of polyamides [22]. The identification of the degradation mechanism might be a key factor to limit side reactions occurring during polymerization.

There have been a significant number of papers released regarding

side reactions during polyamide synthesis. For example, Flannigan et al. [23] reported the ethylation of amine groups by the ester group of diester functional monomer during ester-amide interchange melt polycondensation. The research of Hellmann et al. [23] and Malluche et al. [24] confirmed Flannigan's findings and further investigated the kinetics of those side reactions occurring during both melt polycondensation of dicarboxylic acids and melt polycondensation of diesters with diamines [24,25].

Simultaneously, the hydrolytic degradation processes of carbohydrate-derived compounds have been investigated. The group of Muñoz-Guerra [8,11,13,26] prepared complex research regarding the biodegradability and hydrolytic degradation of (co)polyesters prepared from biacetalized alditols and aldarates. Methylene acetal moieties in the polymer backbone are stable during hydrolysis in acidic environment, while the ester linkages are cleaved. While methylene acetal units (e.g. GalXH) are stable in acidic conditions, isopropylidene acetal units (e.g. GalXMe) deprotect easier by acidic hydrolysis in concentrated acids like formic acid or trifluoroacetic acid [27,28].

The previously reported [28] different behavior of the two acetal derivatives during polymerization might be associated with their difference in reactivity. Ogata et al. [29] revealed that different substituents on the α or β carbon of the carboxylic acid significantly influence the reactivity of active esters of dicarboxylic acid during solution polymerization.

It is suspected that during the polymerization the acetal protection might be removed, leaving galactaric acid with free hydroxyl groups in

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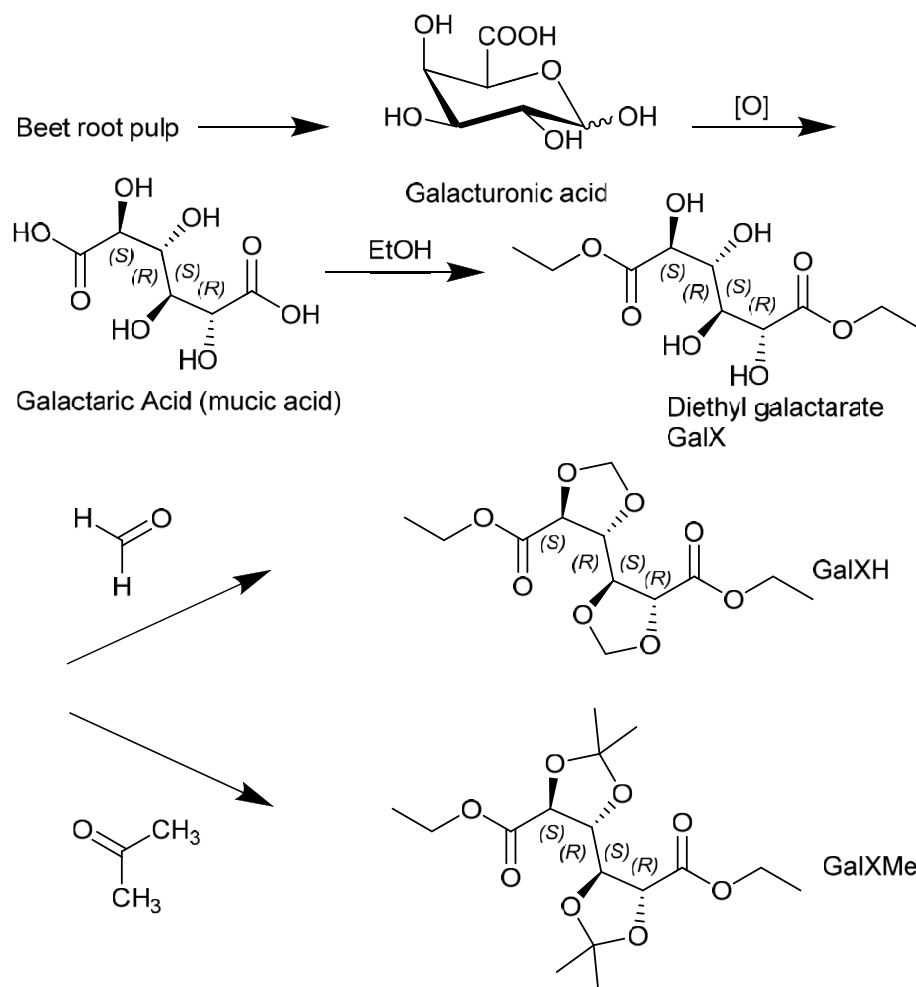


Fig. 1. Global synthesis scheme towards difunctional 2,3:4,5-di-O-isopropylidene-galactarate (GalXMe) and 2,3:4,5-di-O-methylene-galactarate derivatives (GalXH).

the reaction mixture (Fig. 2). As hypothesized in our previous paper [28], this results in multifunctional molecules that act as branching agent/crosslinker. Furthermore, as shown by Kiely et al. in the research investigating the behavior of unprotected galactaric acid and polyamides therefrom, those unprotected hydroxyl species contribute to the formation of cyclic lactones during the synthesis [17,30,31]. Additionally, numerous papers have been released describing the polymerization of monoacetalized tartaric acid [32–35] in which the formation of cyclic 5 member ring imides from amine and tartrates was discovered [32].

The present study focuses on different degradation processes which occur during the melt polycondensation of biacetalized galactaric acid derivatives presented in Fig. 2 with diamines. Both melt polycondensation of dicarboxylic acid GalX salts and melt polycondensation of GalX diethyl esters, will be investigated. A key aspect of the presented study is the degradation of acetal moieties during polymerization and after it is incorporated into the polymer backbone, both thoroughly investigated by the combined GPC, NMR, TGA-MS, LC-MS and Maldi-ToF techniques. Among the complicated mixture of side products which are formed during polymerization, the most important ones were identified and are presented in this paper.

2. Materials and methods

2.1. Materials

Diethyl 2,3:4,5-di-O-isopropylidene-galactarate > 99%, diethyl

2,3:4,5-di-O-methylene-galactarate > 99%, 2,3:4,5-di-O-isopropylidene-galactaric acid > 99% and 2,3:4,5-di-O-methylene-galactaric acid > 99% were delivered by Royal Cosun. 1,6-hexamethylenediamine (HMDA) 98%, benzyl amine (BnA) 99%, Irganox 1330, acetonitrile- d_3 (ACN- d_3), dithranol, NaTFA and KTFA were purchased from Sigma Aldrich and used as received. Silica gel (60–200 μm , 60 \AA), 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), dimethyl sulfoxide (DMSO) 99.7%, DMSO- d_6 and CDCl_3 were purchased from Acros Organics. Tetrahydrofuran (THF), n-hexane, ethyl acetate, acetonitrile (ACN), acetone, chloroform (CHCl_3) and ethanol were purchased from Biosolve.

2.2. Synthetic methods

1,6-hexamethylenediamine-2,3:4,5-di-O-isopropylidene-galactaric acid salt. To a solution of 2,3:4,5-di-O-isopropylidene-galactaric acid (4.35 g, 15 mmol) in ethanol (10 mL) at 50 $^\circ\text{C}$ a solution of 1,6-hexamethylenediamine (1.74 g, 15 mmol) in ethanol (6 mL) was added dropwise. During the addition, a precipitate was formed. The mixture was stirred at 80 $^\circ\text{C}$ for 2 h. The crude product was filtered and recrystallized from an ethanol/water mixture (8/1, v/v) to afford the salt as white crystals (3.83 g, 86% yield) with a melting point of 261 $^\circ\text{C}$.

$^1\text{H NMR}$ (300 MHz, D_2O) δ (ppm): 4.50 (2H, -CH-O-, m), 4.44 (2H, -CH-O-, m), 2.91 (4H, -CH $_2$ -NH $_3^+$, m), 1.58 (4H, -CH $_2$ -CH $_2$ -CH $_2$ -NH $_3^+$, m), 1.42 (6H, -CH $_3$, GalX, s), 1.34 (6H, -CH $_3$, GalX, s), 1.26 (4H, -CH $_2$ -CH $_2$ -CH $_2$ -NH $_3^+$, m).

ATR-IR ν (cm^{-1}): 3500–3000 ν (N-H) NH $_3^+$, 2986 ν (C-H) CH $_3$, 2933

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