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Synthesis and properties of new poly(ether–ester)s containing aliphatic diol based on isosorbide. Effects of the microwave-assisted polycondensation

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Abstract

Microwave irradiation was applied to synthesize to the bulk synthesis of novel poly(ether–ester)s based on diol-ether of isosorbide (**1**) and adipoyl chloride (**2**) or terephthaloyl chloride (**3**). Thus, the poly(ether–ester)s (**4** and **5**) consist partially of isosorbide. In order to check the influence of microwaves and possible specific non-thermal microwave effects, the reactions were comparatively performed inside a thermostated oil bath under similar conditions. The reaction conditions were varied to optimize both yields and molecular weights of poly(ether–ester)s. The reaction proceeded roughly five times faster under microwave irradiation, the polycondensation being almost completed (yields upto approximately 95%) within 5 min to afford a series of novel poly(ether–ester)s based with relatively high average molecular weights (M_w upto approximately 8000). The resulting poly(ether–ester)s were characterized by NMR (^{1}H and ^{13}C), FT-IR spectrometry, SEC measurements and MALDI-TOF mass spectrometry. Thermal properties of the poly(ether–ester)s (**4** and **5**) were investigated by means of differential scanning calorimetry (DSC).

Keywords: Polycondensation; Isosorbide; Poly(ether–ester)s; Microwave activation; MALDI-TOF mass spectrometry

1. Introduction

The majority of polymers used for commercial purposes originates from oil-based monomers. Polymers derived from starch or other carbohydrates are of great interest since these materials are made from entirely renewable resources [1–4]. The direct use of monomeric carbohydrate derivatives is extremely difficult because of a number of hydroxy functionalities in these compounds rendering the synthesis of well-defined products a very difficult task. This problem can be circumvented by using 1,4:3,6-dianhydrohexitols for the synthesis of numerous

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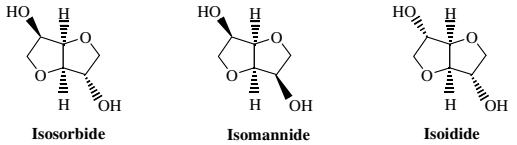
polymers such as polyethers [5–7], polyesters [8–11], polyurethanes [12,13] and polycarbonates [14]. Hexitols and 1,4:3,6-dianhydro hexitols have all four chiral centres, the carbon atoms C-2, C-3, C-4 and C-5. Out of all the possible stereoisomers, there are three that are chiral, namely isosorbide, isomannide and isoidide, these being respectively obtained from glucose, mannose and fructose.



1,4:3,6-dianhydro-D-sorbitol (isosorbide) is prepared by hydrogenation and subsequent dehydration from D-glucose [15,16] (Fig. 1). 1,4:3,6-dianhydro-D-sorbitol (isosorbide) is the most accessible and thus the most studied one [15,16].

Recently, various chiral alcohols linked by ether bridges derived from isosorbide were synthesized by Loupy et al. under economic, easy-to-perform and mild conditions [17]. In the present work, we focus our interest on novel monomers (**1**) (aliphatic chain lengths [$n = 4$]) (Fig. 2). These monomers bear in their molecules two hydroxy groups that are pointing outwards (*exo*) and in opposite directions from the bicyclic system, this rendering them good candidates for polycondensation reactions [17,18].

This work is concerned within the frame of a better utilization and valorization of biomass derivatives and more especially with the novel ether-diols **1** based on isosorbide. We present here the systematic study on polyesters **4** and **5** which are derived partially from renewable resources (Eq. (1)). They were prepared in bulk from the ether-diol **1** and two dicarboxylic acid dichlorides (i.e., adipoyl chloride **2** and terephthaloyl chloride **3**).

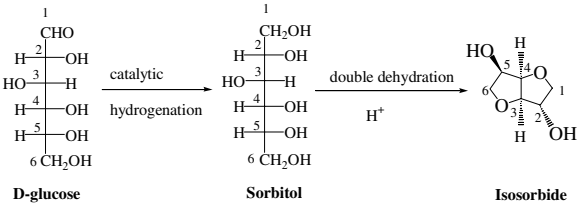


Fig. 1. Two steps for the synthesis of isosorbide from D-glucose [15].

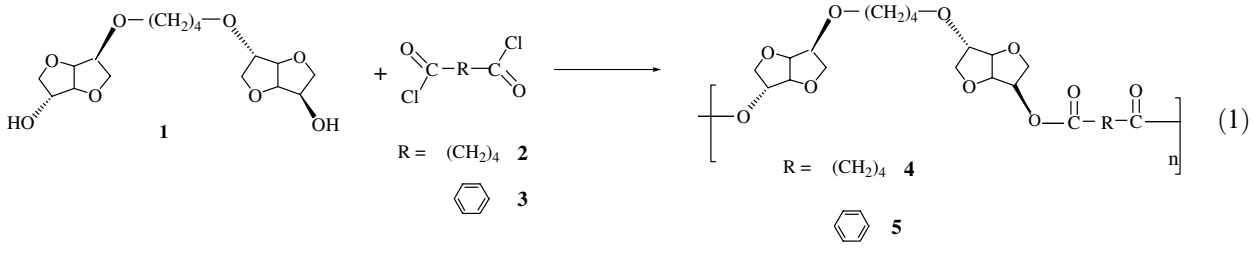
On the other hand, it has been shown recently that microwave (MW) activation in the polymer synthesis allows enhancements in the reactivity as well as selectivity. Moreover, it often results in a substantial reduction of the reaction time, and a net improvement of the yields and of the properties of the final products [19–25,33]. Such method has been utilized here. For the sake of comparison, we performed all the reactions under conventional heating (Δ) with similar reaction conditions i.e., vessels, temperature, pressure, reaction times with even same temperature profiles under both type of activation MW and Δ. To this purpose, the monomode reactor (Prolabo, Synthewave 402), with accurate measurement of temperature by means of infrared detection as well as optical fiber during the reaction course, was used. The reactor allows also adjusting reaction temperature at a constant value by the modulation of emitted MW power and an efficient mechanical stirring [26].

The resulting poly(ether–ester)s (**4** and **5**) were characterized using different complementary analytical methods (^{1}H and ^{13}C NMR, FT-IR, MALDI-TOF mass spectrometry, SEC, DSC).

2. Results and discussion

2.1. Preliminary studies

In general, polyesters can result from the polycondensation reaction between diols and diacids,



(1)