European Polymer Journal 73 (2015) 38–49

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Resorcinol: A potentially bio-based building block for the preparation of sustainable polyesters

Claudio Gioia [a,*], Maria Barbara Banella [a], Micaela Vannini [a], Annamaria Celli [a], Martino Colonna [a], Daniele Caretti [b]

[a] Alma Mater Studiorum – University of Bologna, DICAM, Via Terracini 28, 40131 Bologna, Italy
[b] Alma Mater Studiorum – University of Bologna, CHIMIND, Viale Risorgimento 4, 40136 Bologna, Italy

ARTICLE INFO

Article history:
Received 17 July 2015
Received in revised form 29 September 2015
Accepted 30 September 2015
Available online 3 October 2015

Keywords:
Resorcinol
Sustainable polyesters
Renewable sources
Aromatic polyesters
One-pot polymerization
Structure–property relationships

ABSTRACT

Potentially bio-based aromatic polyesters with a kinked structure based on resorcinol have been successfully prepared. The process involves an optimized reaction between resorcinol and ethylene carbonate: the diol thus obtained was polymerized with several aliphatic and aromatic dicarboxylic acids. The chemical structure and the thermal properties of the new polyesters were analyzed in order to find correlations between structure and properties. All the polymers present a high thermal stability and are mainly amorphous, with a wide range of glass transition temperatures, according to the diacid structures. On the basis of the results it is clear that resorcinol, which can be derived from renewable resources, is a potential bio-based aromatic monomer, suitable to prepare amorphous polyesters containing 1,3 substituted aromatic moieties, for coating and packaging applications.

1. Introduction

In the last few years the increasing need to substitute, or at least lower, the impact of petrol-based compounds on our society led to the development of a variety of innovative, eco-friendly synthetic strategies for the main chemicals and materials [1]. Such approach is actually driven by the possibility to commercialize environmentally sustainable materials with high market penetration. The preparation of renewable aromatic polymers represents today a huge challenge in polymer science, both from the industrial and the academic points of views [2]. One of the main problems to be overcome is connected to the difficulty to find suitable natural sources and processes to obtain renewable aromatic monomers that are usually scarce or difficult to treat. As an example, molecules derived from ligno-cellulosic feedstocks suffer for the presence of multiple functional groups that hinder their exploitation in polyester synthesis [3].

In the field of aromatic polyesters, terephthalic acid (TPA) represents the most exploited aromatic compound; poly(ethylene terephthalate) (PET) is predominant in beverage packaging production, and is also widely used for fibers and as an engineering thermoplastic material. In order to develop sustainable alternatives to the petro-based PET, different processes have been recently reported [4]. In particular, recent patents and papers demonstrate the possibility to obtain TPA from bio-based chemicals such as muconic acid [5], isobutylene (obtained from isobutanol) [6] or limonene [7].

* Corresponding author.
E-mail address: claudio.gioia2@unibo.it (C. Gioia).

http://dx.doi.org/10.1016/j.eurpolymj.2015.09.030
0014-3057/

On the other hand, isophthalic acid (IPA) based polyesters are widely used in several industrial applications such as, for example, in the coating market. They are amorphous materials, given their kinked structure induced by the 1,3-substitution of the aromatic ring. In several cases, isophthalic groups are added to terephthalate polyesters in order to suppress their crystallinity. Moreover, IPA based polyesters provide high thermal stability and increased barrier properties when compared to TPA polyesters. This behavior has been ascribed to the blocked rotation along the polymer main chain due to the 1,3-substitution [8]. However, up to date only a route for the preparation of sustainable polymers based on isophthalate monomers has been reported in the literature [9,10]. In particular, the method starts from bio-isoprene and bio-acrylic acid to produce bio-terephthalic and isophthalic acids, even if the aim is the production of TPA, whereas IPA is only a secondary product.

Therefore, new routes are to be rapidly found to produce sustainable aromatic monomers with non linear structures (e.g. 1,3-substitution) for the preparation of non-crystalline polyesters in view of applications in the coating and packaging sectors.

With this purpose, the present paper aims at exploiting resorcinol that could be an interesting structure because it features two OH groups with a 1,3 pattern and therefore gives rise to kinked polymeric structures. Moreover, although its main production is currently petrol based, at present several different pathways to obtain bio-based resorcinol are reported in the literature [11–14]. Resorcinol can be produced from biomass through fermentative and/or chemical processes. In particular it can be prepared from catechins by fermentation [11] or, more commonly, from glucose following two routes:

– via inositol: from glucose inositol can be obtained by fermentation [12] to be subsequently chemically converted into 1,3,5-benzenetriol (commonly named phloroglucinol) [13]. 1,3,5-Benzenetriol can be reduced to resorcinol (Fig. 1);
– via triacetic acid lactone (Fig. 2): [14] triacetic acid lactone can be prepared from glucose by fermentation and can be converted into the corresponding methyl ether. The methyl ether is transformed into 1,3,5-benzenetriol methyl ether that can be converted into resorcinol directly or passing by 1,3,5-benzenetriol as an intermediate.

The role of resorcinol in material science is usually related to the synthesis of polyarylated materials that involves harsh reaction conditions due to the poor reactivity of phenolic groups compared to aliphatic hydroxyl moieties. For this reason, in order to develop resorcinol based monomers with enhanced reactivity, a chemical functionalization is required. Then, 1,3-bis (hydroxyethoxy)resorcinol (HER), derived from resorcinol and ethylene carbonate (ETC) (Fig. 3), can be an interesting monomer, whose synthesis is described in the literature [15,16].

It is also notable that ETC is used in several environmental friendly processes such as the phosgene free production of bisphenol A polycarbonate [17–19] and can be obtained from renewable resources [20].

Surprisingly, the use of HER in the synthesis of polyesters has been poorly investigated. In particular, Vijayakumar et al. [21] have performed the synthesis and characterization of saturated and unsaturated polyesters based on HER and adipic acid or maleic anhydride in order to study their thermal degradation (Fig. 4).

In a patent [22] HER has been polymerized with 1,3-phenylenedioxydiacetic acid obtaining a polymer with a low O_2 and CO_2 permeability that could be useful in food and beverage packaging. This patent confirms the importance of 1,3 substituted aromatic compounds for the synthesis of high barrier polymeric materials. The fact that meta-linkages derived from resorcinol give high barrier properties is reported in literature [23]. Jabarin and Fehn [24,25]. Go [26] and Takahashi et al. [27] claim that HER inserted in polyesters or co-polyesters gives them high gas barrier properties. However, for all patents it was reported that a few diacids in combination with HER were used. To the best of our knowledge there is no paper describing the preparation and characterization of a wide set of aromatic polyesters based on HER, and comparing their properties with those of the petro-based counterparts.

For this reason, the present paper aims at reporting a detailed optimization of the HER synthesis with respect to that reported in the literature, along with its polymerization with different diacids and diesters mainly deriving from renewable resources, including a one-pot synthetic procedure from resorcinol, ETC and diacids. The chemical and thermal characterization of the polymers are also described.

2. Experimental

2.1. Materials

Resorcinol (RES), ethylene carbonate (ETC), potassium carbonate, succinic acid (SA), 1,4-cyclohexanedicarboxylic acid dimethyl ester (100% *trans* isomer), 1,4-cyclohexanedicarboxylic acid (65% *trans* isomer), dimethyl isophthalate (DMI),

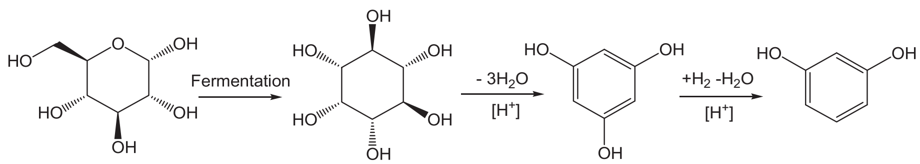

Fig. 1. Resorcinol synthesis from glucose via inositol.