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Synthesis of castor oil-derived polyesters with antimicrobial activity

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ABSTRACT

This work aims at preparing new castor oil-derived polyesters with antibacterial activity. Ricinoleic acid and 10-undecenoic acid, derived from castor oil, were successfully used for this purpose. Firstly, an unsaturated homopolymer, derived from the self-polycondensation of ricinoleic acid, and its copolymers with poly(butylene succinate) were synthesized and resulted to be characterized by a remarkable biocidal activity against *Staphilococcus aureus* and a medium efficiency against *Escherichia coli*. Secondly, a PE-like aliphatic polyester, the poly(hexamethylene succinate), has been modified at the chain ends with the presence of unsaturated units of 10-undecenoate. This polymer was characterized by a low biocidal activity, mainly against Gram-positive bacteria. Furthermore, for both these polymeric systems the presence of the double bonds has been successfully exploited to covalently link an antimicrobial molecule, a vinyl imidazolium salt, which significantly improved the biocidal performances of the final polymers. Therefore, a general method to link molecules to the double bonds of PRA and undecenoate units and to insert new specific functionalites to the castor oil-derived polyesters is here developed.

1. Introduction

In recent years, industrial and academic research are strongly involved in the replacement of petro-based materials with renewable substitutes. In the wide range of possible bio-based monomers, plant oils are among the most promising candidates as economical and renewable source of many monomers for bio-polymer production [1–3]. More specifically, castor oil, derived from the beans of the castor plant, *Ricinus Communis*, of the *Euphorbiaceae* family, can be considered the starting biomass for the development of a platform of chemicals and bio-polymers, as already done for other biomass, such as sugars.

Castor oil contains approximately 85–90 wt% of triglycerides of ricinoleic acid, which could be a precursor for the synthesis of interesting materials thanks to the presence of hydroxyl and carboxyl groups, as well as a Δ9 unsaturation. Scheme 1 summarizes the biomass source of ricinoleic acid and some potential applications in the polymeric field.

Poly(ricinoleic acid) (PRA) with low molecular weight ($M_n \approx$ 1000–3000 g/mol) was obtained by Krasko and Domb [4], in the presence of toluene as solvent and *p*-toluenesulfonic acid as catalyst, and by Slivniak and Domb [5], by a two-step polycondensation procedure conducted for 15 h at 180–150 °C. Only by enzymatic catalysis Ebata et al. [6] were able to prepare PRA at high molecular weight ($M_w \approx$ 100,000 g/mol). The PRA produced was a viscous liquid, with a glass transition temperature of about −75 °C, i.e. significantly low, indicating a very flexible chain

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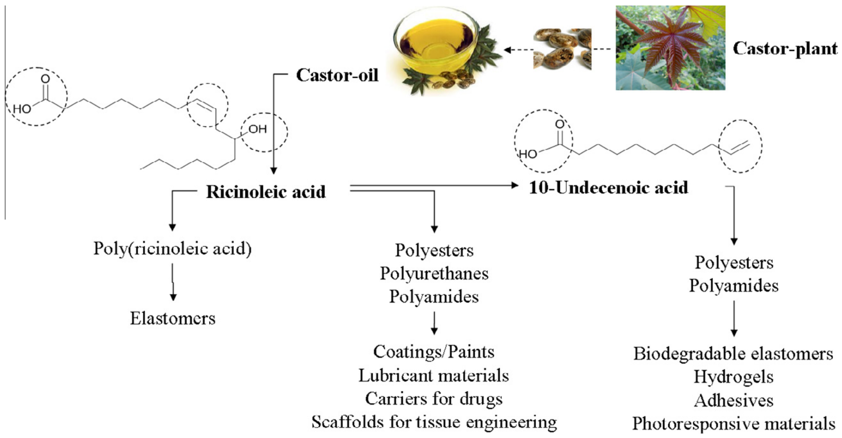

Scheme 1. Biomass source of ricinoleic acid and some potential applications in the polymeric field.

with poor mechanical performances; additionally it can be biodegraded by activated sludge [6]. The presence of the double bond along the chains was exploited for curing reactions to obtain a crosslinked PRA used as soft material, such as elastomer [6,7]. Moreover, units of ricinoleic acid have been incorporated in copolymers with lactic acid [8] and sebacic acid [9–11]; ricinoleic acid-based poly(ester-anhydride) have also been studied [4,12,13].

It is noteworthy that many articles describe the use of ricinoleic acid in biomedical field as drug delivery systems, above all in copolyesters with sebacic acid [4,9,10,12,13]. Moreover, literature also reports some data concerning the antibacterial activity and the combined analgesic and anti-inflammatory effect of the extract from *R. Communis* seeds [14,15], and also of some derivatives of ricinoleic acid [16]. Other applications include the use in the coating industry [17], as environmentally friendly lubricant materials [18], as soft segment in the preparation of segmented polyurethanes [3] and in polylactide blends in order to improve the toughness of pristine polymer, which has many commercial uses [19]. Some patents reported also the use in polyamides as additives for paints, inks or drilling fluids [20,21].

By pyrolysis of ricinoleic acid under vacuum conditions, 10-undecenoic acid, a fatty acid with a double terminal bond, is obtained [22]. It can be used as a substrate to produce poly(3-hydroxyalkanoate) with a wide range of applications including biodegradable elastomers, hydrogels and adhesives [23]. Microbial bioelastomers based on soybean oil and 10-undecenoic acid are also reported by Hazer et al. [24]. An interesting application as photoresponsive materials can be found in a new class of highly substituted α,ω-diene amides, reported by Kreye et al. [25]. In addition, 10-undecenoic acid methyl ester is used to enhance the properties of some aliphatic polyesters, which has the advantage of biodegradability but poor thermal performances [26].

The production of bio-polymers with functional properties is an upgrading of the castor oil valorization. Actually it is widely recognized the pressing need for the development of green and sustainable processes for the conversion of renewable biomass to commodity chemicals and this is one of the hottest subject on the road to a more sustainable bio-based economy.

In view of such considerations, the preparation of unsaturated bio-polyesters based on ricinoleic acid or containing units derived from 10-undecenoic acid, has many interesting features, not only due to the achievement of green materials, but also to the potential antibacterial activity of such polymers. Indeed, not only ricinoleic acid derivatives can have the same bactericidal properties as ricinoleic acid but the double bonds, located along the macromolecular chains or at the chain ends, are also suitable to covalently link bioactive molecules, which can impart this activity to the bulk material.

Consequently these polyesters, fully bio-based, could be suitable for a wide range of applications, such as smart packaging and membranes for filtration.

During the present study different macromolecular structures, reported in Scheme 2, were built and characterized starting from ricinoleic acid and methyl 10-undecenoate: the homopolymer PRA, some PRA-based copolyesters with different composition and telechelic derivatives of poly(hexamethylene succinate) with methyl 10-undecenoate at the chain ends. Finally, the unsaturated units were used to covalently link 3-hexadecyl-1-vinylimidazolium bromide (VIB), a molecule known for its antibacterial activity [27]. The biocidal activity of all the samples prepared was assessed towards *Staphilococcus aureus* and *Escherichia coli*. Correlations between chemical structure and efficiency in bacteria mortality are discussed.

2. Experimental

2.1. Materials

1,4-Butanediol (BD), 1,6-hexanediol (HD), dimethyl succinate (DMS), succinic acid (SA), methyl 10-undecenoate (U), ricinoleic acid (RA), 1-vinylimidazole, hexadecyl bromide, titanium tetrabutoxide (TBT) and Irgacure 651 were purchased from Aldrich Chemical. Components of Nutrient Broth (NB, peptone 5 g/l, beef extract 3 g/l, pH 6.8) used for microbiological analyses were supplied by Merck. Agar and phosphate buffered saline (pH 7.0) were