



PEG-modified poly(10,11-dihydroxyundecanoic acid) amphiphilic copolymers. Grafting versus macromonomer copolymerization approaches using CALB



Carmen Valverde, Gerard Lligadas, Juan C. Ronda*, Marina Galià, Virginia Cádiz

Departament de Química Analítica i Química Orgànica, Universitat Rovira i Virgili, Campus Sescelades Marcel·lí Domingo 1, 43007 Tarragona, Spain

ARTICLE INFO

Keywords:

Polyesters
Hyperbranched polymers
Renewable resources
Enzymatic polycondensation
Amphiphilic polymers
Polymer grafting

ABSTRACT

The synthesis of a partially renewable hydroxyl hyperbranched polyester: poly(10,11-dihydroxyundecanoic acid) (PDHU), by polycondensation using CALB as catalyst, has been described. The synthesized polymers were structurally characterized in detail, using model compounds previously synthesized, by ^1H , ^{13}C and ^{19}F NMR. The synthesis of amphiphilic copolymers by incorporation of mPEG moieties and utilizing CALB, was carried using two methods: by copolymerization of mPEG-OH and 10,11-dihydroxyundecanoic to produce block hyperbranched copolymers, and grafting onto hydroxyl groups of linear and hyperbranched PDHU, mPEG containing carboxylic acid. The microstructure of block and grafted copolymers was determined in detail by NMR spectroscopy by using models and ^1H - ^{13}C heteronuclear bidimensional correlations. The self-assembly of these amphiphilic polyesters form well-defined multimolecular micelles ranging 100–300 nm in very diluted aqueous solutions, showing potential application in drug delivery among other applications.

1. Introduction

The development of polymers that are sustainable by combination of environmental, societal, human health and economic perspectives is a major challenge in polymer science. The key to shifting to sustainable alternatives will be to obtain both existing and new low cost polymers with competitive performance properties from renewable resources [1]. Nowadays, the interest in polymers from renewable resources has been witnessing an incessant growth in both academic and industrial communities [2,3]. The situation has advanced to such extreme that it does no longer need the arguments previously put forward to justify its relevance. Among available renewable resources, vegetable oils and derived fatty acids represent a promising feedstock for the polymer industry, owing to their abundant availability, relative low cost and inherent degradability. Castor oil is one of the most valuable choices. Their high versatility and exclusion of alimentary sector convert this material in a good candidate to explore new routes to obtain biopolymers. 10-Undecenoic acid is available from the pyrolysis of castor oil, and it is a key substrate in polymer chemistry for the synthesis of precursors for the preparation of sustainable materials [4].

The synthesis of vegetable oil-based linear polyesters has been extensively studied in the last years [5–10], including our group that has extended the use of 10-undecenoic acid to the synthesis of

functionalized polyesters from specialty monomers [11–14]. However, only limited attention has been dedicated to hyperbranched polyesters derived from plant oils. Related examples have involved the polycondensation of AB_n -type precursors [15–17]. Oil-based polyesters bearing hydroxyl reactive pendent groups have also been reported [14,18–21]. Interestingly, a linear hydroxyl functionalized hydrophobic polyester chain was modified to obtain a macro-chain transfer agent on which grafting from with bio-based acrylates was performed to prepare amphiphilic grafted copolymers [21].

For many years, postpolymerization modification has been perceived as unavoidable, when one is unable to synthesize a polymer by direct polymerization. However, as it has become apparent nowadays, the reasonable combination of efficient chemical transformations with macromolecular structures can provide a profusion of materials with irresistible properties, myriad functionalities, and elaborated architectures [22].

By self-assembly or co-assembly of amphiphilic block copolymers have been prepared nanosized micelles with a core-shell architecture in a selective solvent and have attracted increasing attention for drug delivery [23–26]. The hydrophobic core serves as a natural carrier environment for hydrophobic drugs, and the hydrophilic shell stabilizes the particles in aqueous solution [27]. Micelles can be classified as simple and complex according to their structure and size. Primary

* Corresponding author.

E-mail address: juancarlos.ronda@urv.cat (J.C. Ronda).

<https://doi.org/10.1016/j.eurpolymj.2018.09.032>

Received 30 July 2018; Received in revised form 7 September 2018; Accepted 17 September 2018

Available online 18 September 2018

0014-3057/ © 2018 Elsevier Ltd. All rights reserved.

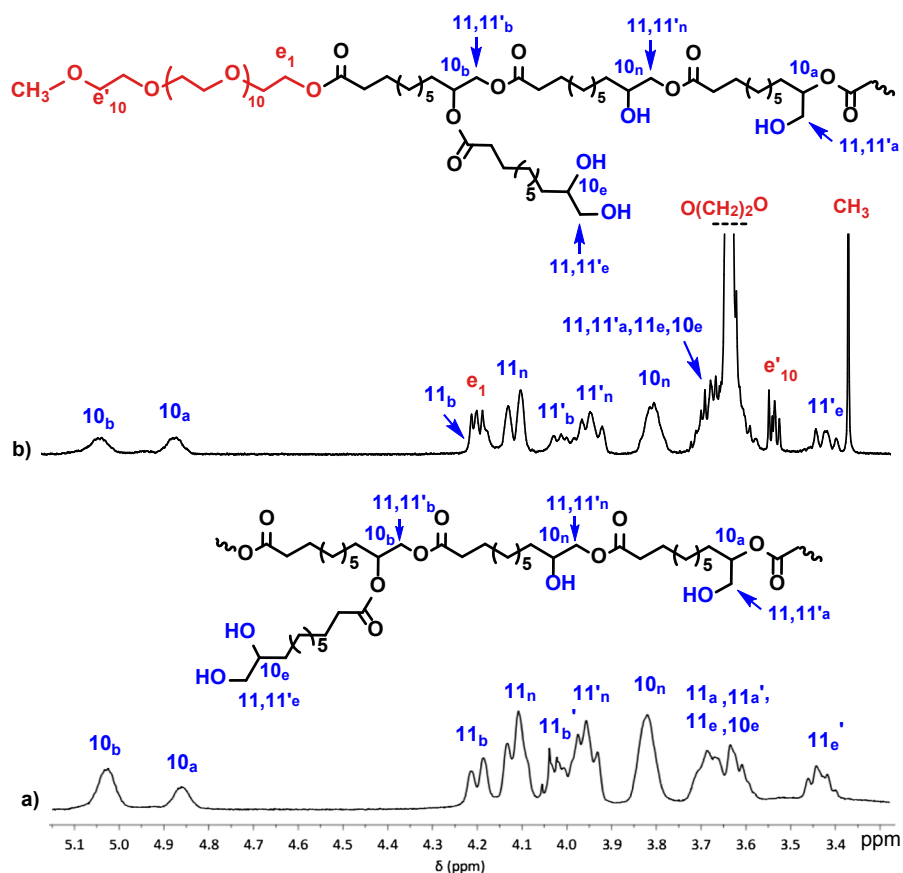


Fig. 1. Region between 5.2 and 3.2 ppm ^1H NMR spectrum of (a) PDHU and (b) mPEG₁₂-b-PHDU₉, with the corresponding assignments in a representative structure.

micelles are generally smaller than 50 nm whereas complex micelles, larger in size (higher than 100 nm) are usually formed by secondary aggregation of primary micelles [28].

Simple multimolecular micelles are generally formed by primary aggregation of block copolymers due to the microphase separation in selective solvents. The resulting self-assembled materials usually lack of the necessary thermodynamic stability when changes in concentration or other parameters as temperature or ionic strength occur, producing disassemble and the formation of free polymeric chains. These drawbacks can be overcome by core or shell crosslinking approaches endowing micelles with excellent structural stability although crosslinking generally compromises the final biodegradability. Alternatively, design of amphiphilic polymers with certain architectures such as dendritic, hyperbranched, star or heterografted brush-shaped molecules, provides an alternative strategy to prepare stable polymeric micelles. Due to their unique architecture can form unimolecular micelles with excellent stability regardless of the high dilution condition and other microenvironment changes [29].

Amphiphilic hyperbranched polymers is one type of materials that have been widely used for unimolecular micelle preparation [30]. On contrary to other architectures such as dendritic polymers, these hyperbranched polymers can be synthesized following convenient one-step synthesis on a large scale and good yields, by simply polycondensation of AB_x monomers or ring opening polymerization of latent AB_x monomers [31]. Strategies for preparing amphiphilic hyperbranched polymers include incorporation of hydrophobic components into a preformed hydrophilic polymeric chain, which essentially renders a block copolymer, or the modification of the hydrophobic hyperbranched core by the incorporation of multiple hydrophilic arms rendering graft polymers [29,32]. In this sense, PEGylation has for a long time been known as a simple and effective approach to provide the amphiphilic structures, enhanced water compatibility and self-

aggregation properties [33,34].

Both, amphiphilic PEG-derived block copolymers and grafted polymers can associate in the appropriate solvent to produce micellar architectures. Intramolecular assembly will lead to unimolecular micelles while intermolecular assembly will induce to multimolecular micelles. Moreover, in contrast to linear block copolymers, block hyperbranched and grafted polymers enable to tune the different associate structures by controlling branching degree or grafting density. Some examples of PEG-derived hyperbranched amphiphilic polyesters have been reported in the last decade [35–37] including one that uses the environmentally friendly CALB as catalyst [38].

In this report, we describe the synthesis and characterization of a renewable hydroxyl hyperbranched polyester: poly(10,11-dihydroxyundecanoic acid) (PDHU), by polycondensation using CALB as catalyst. Moreover, different approaches were used for the synthesis of partially renewable amphiphilic copolymers by incorporation of methoxypolyethyleneglycol moieties (mPEG_n). First, copolymerization of mPEG_n-OH of different lengths and 10,11-dihydroxyundecanoic was used to produce block hyperbranched copolymers. Moreover, mPEG containing carboxylic acid groups (mPEG₂OCH₂COOH and mPEG₃OOC(CH₂)₂COOH) was attached to hydroxyl groups of linear and hyperbranched PDHU to render different grafted polymers. The self-assembly and micellar behaviour of these amphiphilic structures was investigated.

2. Experimental

Synthesis and characterization of monomers, model compounds and other reagents is collected in the supporting information (SI.1 and SI.2).

Download English Version:

<https://daneshyari.com/en/article/11031192>

Download Persian Version:

<https://daneshyari.com/article/11031192>

[Daneshyari.com](https://daneshyari.com)