



Environment-friendly synthesis of amphiphilic polyester-graft-poly(vinyl alcohol)



Nadia Guerrouani, Benoit Couturaud, André Mas*, François Schué, Jean-Jacques Robin

Institut Charles Gerhardt, Montpellier, UMR5253 CNRS-UM2-ENSCM-UM1, Equipe Ingénierie et Architectures Macromoléculaires, Université Montpellier 2 – Bât 17 – cc1702, Place Eugène Bataillon, 34095 Montpellier cedex 5, France

ARTICLE INFO

Article history:

Received 8 November 2012

Received in revised form 14 February 2013

Accepted 17 February 2013

Available online 26 February 2013

Keywords:

Graft copolymers

Amphiphilic copolymers

Ring opening polymerization (ROP)

Poly(vinyl alcohol)

Poly(L-lactide)

ABSTRACT

Experimental conditions for the synthesis of poly(ϵ -caprolactone)-graft-poly(vinyl alcohol) (PCL-g-PVA) and poly(L-lactide)-graft-poly(vinyl alcohol) (PLLA-g-PVA) via a PVA/MgH₂ macroinitiator were optimized. Heat stability of PVA (99% hydrolyzed) in L-lactide (L-LA) melt was studied by DSC, TGA to lower the reaction temperature and time in order to avoid degradation. Thus, no degradation of copolymers occurred and ¹³C NMR study showed that L-lactide was incorporated in graft chains as isotactic poly(L-lactide) without racemisation for 140–160 °C, up to 25 h, L-LA/PVA ratio in the range 3–12. Such synthesis using non-toxic catalyst and reactants in a solvent-free medium can be described as environment-friendly. Amphiphilic behavior of copolymers was studied in aqueous solution according to their chemical structures: critical micelle concentration CMC (0.03–0.5 g L⁻¹), average diameter of micelles (80–150 nm), surface tension γ_{CMC} (46–63 mN m⁻¹), hydrophilic to lipophilic balance HLB (Griffin definition 4–7), and also from cast films: surface energy γ_s (36–50 mJ m⁻²). This environment-friendly process is suitable for the use of graft PVA copolymers in biomedical area for investigations under micelle applications.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Increasing interest on block and graft copolymers arises mainly from their associative properties in solution as a consequence of their amphiphilic molecular structures.

Poly(ethylene glycol) (PEG) is the most used hydrophilic block, it was notably linked to biocompatible and biodegradable aliphatic polyesters such as polylactide (PLA) and polycaprolactone (PCL) as hydrophobic blocks. Many research groups are interested particularly in preparing PEG-based hydrogels for biomedical and pharmaceutical applications [1,2]. PEG led to diblock and triblock copolymers with variable hydrophilicity/hydrophobicity balance which affects the physical properties required to form micelles in water and may have effect on the stability and hydrolytic degradation of PLA and PCL blocks [3,4].

Recently poly(vinyl alcohol) (PVA) attracted much attention as hydrophilic main chain because it offers more possibility of varying the hydrophilic/hydrophobic balance by means of the number and the length of hydrophobic side chains. In this way, the properties of PVA based graft copolymers should be more easily modulated, however only a few detailed studies have been performed. Hydrogels and microspheres for drug encapsulation made of PVA graft copolymers were investigated [5,6]. The poor solubility of PVA in organic solvents limited the graft-polymerization process of aliphatic polyester chains, furthermore the poor solubility of copolymers in water limited the exchange of organic solvent against water to prepare hydrogels from copolymers solutions. It has been shown that the stability of hydrogels based on grafted PVA increased with decreasing hydrophilicity of the copolymer [7], the stability of micelles also increased for copolymers containing PVA block with high syndiotacticity [8] pointing out the importance of the stereoregularity of the structure on the amphiphilic behavior.

* Corresponding author.

E-mail address: andre.mas02@univ-montp2.fr (A. Mas).

The development of syntheses which makes it possible to control block length and amphiphilic properties is essential. PEG based amphiphilic copolymers have been extensively studied since PEG is a very available water soluble polymer. Generally the synthesis of PEG copolymer proceeds in two stages. First the anionic macroinitiator is formed from di-hydroxylated PEG and a metal derivative catalyst, then ring opening polymerization (ROP) of ϵ -caprolactone or lactide occurs leading to polyester blocks. Same procedure using anionic macroinitiator can be adapted to graft the PVA chain. Nevertheless the special properties of PVA such as poor solubility and thermal stability, have to be considered.

Many organic metallic compounds derived from heavy metals are effective for the synthesis of polyesters but they are toxic [9]. Stannous octoate (SnOct_2) is the most commonly used metal based catalyst and is approved by the US Food and Drug at level not exceeding 1% by weight of the resin used in coatings that are intended for contact with food. It was also approved for internal use for the human body however some moderation is cautiously recommended for its use for surgical and pharmacological applications. Nevertheless many authors consider that organometallic tin compounds are characterized by high toxicity particularly for the use of obtained polymers in biomedical applications [9].

SnOct_2 is currently used in industry because the initiated polymerizations are fast and yield high molecular weight polymers with no detectable residual monomer and low transesterification reactions. Polymerizations are carried out generally in toxic solvent as toluene and it is experimentally impossible to remove all the catalyst and side tin compounds from the polyesters by purification methods involving dissolution and precipitation. The residual tin in polylactide is about 300–400 ppm.

Zinc based catalysts are more and more used in the ROP of lactones because it seems that they are less toxic than tin based catalysts and the residual level is lower [9]. Also, in the last decade considerable research effort has been expended to develop catalysts based on nontoxic metal as Ca, Fe, and Mg [10–13].

Moreover, to avoid the presence of metal ions in the final product, many teams have reported the use of organocatalysts derived from pyridine, phosphazene, phosphine and N-heterocyclic carbenes [14]. The rates and selectivities of organocatalysts are competitive with the most active and selective metal based catalyst. Different mechanisms of enchainment are engendered by the different classes of organocatalysts and provide new opportunities for the controlled synthesis of macromolecules. Even if most studies report the synthesis of polyesters in solution, the use of a stable imidazolium-based catalyst formed through a simple acid–base reaction between an imidazole base and one equivalent of trifluoroacetic acid, was reported recently for the polymerization of lactide in bulk [15]. ROP was also investigated by using enzyme catalysts such as lipases which are environmentally highly advantageous [16]. However the high cost and large quantity of enzyme required for the polymerization strongly disturb any industrial development.

In a preliminary work, we reported the use of magnesium hydride (MgH_2) as a new catalyst containing an environmental friendly metal for the ROP of ϵ -CL and L-LA [17,18]. MgH_2 was selected because it is well known that magnesium is involved in human metabolism, thus non-toxic residual impurities can be left in copolymers. In the present work, the process already performed for the synthesis of block copolymers from PEG, is extended and optimized to the synthesis of PCL-g-PVA and PLLA-g-PVA under environmentally conditions i.e. non-toxic catalyst and reactants in a solvent-free medium, considering the great difference in thermal properties of PEG and PVA. More particularly, the thermal behavior of PVA in presence of L-LA was studied and optimized conditions for temperature and time during melt process were investigated to avoid any thermal degradation. Suitable experimental conditions were also highlighted by a ^{13}C NMR study to avoid the racemisation of L-LA units incorporated in copolymers.

The amphiphilic properties of copolymers were evaluated via the determination of wettability, surface energy of cast films and the hydrophilic to lipophilic balance (HLB). The micellar behavior of copolymers in aqueous phase was investigated by means of surface tension measurements, critical micelle concentration (CMC) and dynamic light scattering (DLS). Changes in properties were discussed in relation to the experimental conditions of the synthesis of copolymers and their structures. Amphiphilic properties were compared to those of triblock PEG copolymers and graft PVA copolymers with similar structures recently described in literature.

2. Materials and methods

2.1. Materials

Di-hydroxy-terminated poly(ethylene glycol) (PEG) ($M_n = 2000$ and $10,000 \text{ g mol}^{-1}$) was purified by dissolution in chloroform and precipitation in diethyl ether then rigorously dried. Poly(vinyl alcohol) (PVA) ($M_w = 41,000 \text{ g mol}^{-1}$, $M_n = 28,000 \text{ g mol}^{-1}$, 99% degree of hydrolysis) was rigorously dried at 100°C in vacuo, ϵ -caprolactone (CL, b.p. $96\text{--}97.5^\circ\text{C}/10 \text{ mmHg}$) was dried on CaH_2 and distilled, chiral lactide (L-LA, m.p. $92\text{--}94^\circ\text{C}$) was purified by crystallization from dried toluene then sublimated, magnesium hydride (MgH_2) was used as received. All chemicals were provided by Sigma Aldrich.

2.2. Synthesis of copolymers

Suitable experimental conditions for the synthesis of graft PVA in the melt were based on a previous work from our laboratory focused on the synthesis of triblock PEG copolymers [17]. First syntheses were carried out using CaH_2 and MgH_2 as catalysts under vacuum as general required method for anionic polymerization. In a second time all syntheses were carried out using only MgH_2 under argon in monomer melt because vacuum process did not lead to better yield and higher purity of products. Moreover, the use of vacuum could restrain any future industrial development. Indeed MgH_2 reacts slightly more weakly

Download English Version:

<https://daneshyari.com/en/article/10609541>

Download Persian Version:

<https://daneshyari.com/article/10609541>

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