



# Crystalline and spectroscopic characterization of poly(2-aminoethyl methacrylate hydrochloride) chains grafted onto poly[(R)-3-hydroxybutyric acid]

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## ABSTRACT

The present study is aimed to investigate the degree of crystallinity of poly(3-hydroxybutyrate) P(3HB) grafted with poly(2-aminoethyl methacrylate hydrochloride) (PAEMA) chains using WAXS, micro Raman, and FTIR spectroscopy. The samples were obtained by radiation induced graft polymerization of the monomer in the substrate using different solvents for comparison. The results of crystallinity are consistent with those obtained of lower crystallinity in grafting copolymer relative to the substrate P(3HB). The low crystallinity is directly related to the increase of the degree of grafting, meaning that although the P(3HB) amorphous region is grafted, the crystalline zone is also affected in some extent by the grafting process and the environment of the new molecule. Three different methods were surveyed to determine the variation of crystallinity degree with the grafting degree. It is shown that all methods provide linear relationships between these variables, but WAXS method was found more acceptable than the others (FTIR and Raman). A detailed characterization of the vibrational bands characteristic of amorphous and helical crystalline structure of the grafting copolymers are also highlighted.

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## 1. Introduction

Poly(3-hydroxybutyrate) is a semicrystalline naturally occurring biopolymer that is well known as the carbon reserve of a large variety of microorganisms [1,2]. This polymer is the most-popular member of the polyhydroxyalkanoates family, and it was discovered by Lemoigne more than eight decades ago [3]. This is a thermoplastic material often compared with polypropylene but with the added advantage of being biocompatible, biodegradable and thermally more stable [4–6]. The cited characteristics are complementary with its suitable mechanical properties to be used in biomedical engineering and bone applications [7–9]. On the other hand, P(3HB) and its copolymers (P(HB-co-HV)) have also

been used in the field of medicine in drug delivery systems and scaffolds [10,11]. In spite of the great mentioned properties of P(3HB), it also has some limitations that can be of some concern. The former is the lack of active functional groups in the P(3HB) structure, and the latter its high crystallinity [12]. In particular, the crystallinity is important because the more crystalline the material is, the more brittle it becomes, which is not desirable for commercial applications [13]. Several modifications of P(3HB) have been proposed in order to improve the mentioned drawbacks [14]. Toughness can be enhanced by modifications of the molecule that involves physical or chemical changes [15]. Physical changes, such as blends, are used to obtain novel materials, like plasticized P(3HB), with specific characteristics for specific application, based on its high thermal stability [16,17]. Chemical changes imply the formation of a new product [18,19], where the grafting reaction has risen as one of the most efficient ways to modify chemically the poly(3-hydroxybutyrate) [20,21]. Amine and carboxylic groups are

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the largest studied functional groups grafted onto the biopolymer [22,23].

Recently, amine groups (aminoethyl methacrylate hydrochloride (AEMA)) were introduced, by grafting, onto poly(3-hydroxybutyrate-co-hydroxyvalerate) membranes by gamma radiation using several concentrations of the monomer [24]. However, the graft reaction of the AEMA oligomers onto P(3HB) powder, and the study of the structure and crystallinity of the graft copolymers, has not been reported. Additionally, as FTIR and Raman are recognized as suitable techniques for polyhydroxyalkanoates crystallinity studies, several work involving the isodimorphism, and degree of crystallinity are revealed [13,25,26].

Moreover, the study of the structure, crystallinity, dispersibility, the changes in configuration and conformation with molecular dynamics, the temperature-dependent variation of poly(3-hydroxybutyrate) and its copolymers or blends, have been extensively investigated by: X-ray diffraction [27–29], Fourier-transform infrared [30–33], Raman [34–36], near-infrared [37] and Terahertz (THz) spectroscopy [38,39].

For example, the WAXD research of P(3HB-co-HHx) allowed to corroborate the inter- & intra-molecular interaction of the carbonyl and methyl groups, which is due to their closeness, and also surveyed the only thermal expansion of the “a” side of the lattice [27]. The X-ray diffraction was furthermore used to investigate the dependence of P(3HB) and poly(L-lactic acid) with the temperature, which revealed the crystallization disorder affectation of the studied blends around the melting point [28]. Besides, it was possible to probe with this technique that as temperature increases, the degree of crystallinity in the poly(3-hydroxybutyrate) varied in the P(3HB)/cellulose acetate butyrate blends [29]. In addition, the crystallinity, dispersibility and the details of the structural changes of different blends such as P(3HB)/poly(L-lactic) (PLLA) ranged from 20 to 80 wt.% [30] and P(3HB)/poly(4-vinyl phenol) (PVPh) have confirmed the P(3HB)/PLLA immiscibility and the decrease of the poly(3-hydroxybutyrate) crystallinity with PVPh increase [31]. Moreover, Unger examined the changes on the carbonyl FTIR region when P(3HB) is blended with poly( $\epsilon$ -caprolactone) to obtain information of the crystalline and amorphous absorption band by using two-dimensional correlation spectroscopy (2DCOS) [33]. Likewise, the cellulose acetate butyrate blends with P(3HB) was studied by near infrared imaging (NIR). The authors have investigated the melt isothermal crystallization also supported by infrared spectroscopy [37]. It has been previously explored in deep CH $\cdots$ O hydrogen bonding of these polyesters [34–36] and, recently, the terahertz two-dimensional correlation spectroscopy has been performed by monitoring the evolution of both THz and 2DCOS [38].

Nevertheless, the topic over PHA grafting copolymers has been barely studied. Therefore, this paper describes the results of the syntheses of radiation induced graft polymerization of AEMA onto powder P(3HB) in different solvent environment and discusses the determination of crystallinity degree of the grafting products by using wide angle X-ray diffraction, micro Raman, and FTIR spectroscopy.

## 2. Materials and methods

### 2.1. Materials

Poly(3-hydroxybutyrate) (from Sigma–Aldrich) was purified by precipitation in acetone from chloroform solutions. The solvents: acetone (S5), chloroform (S4), ethyl acetate (S3), hexane (S2), and ethanol (S1) were used as received. Acetic acid media (S6) and the monomer, 2-aminoethyl methacrylate hydrochloride (Sigma–Aldrich) were used without further purification. All chemicals were analytical grade.

### 2.2. Methods

#### 2.2.1. Synthesis

The synthesis experiments were conducted by the simultaneous irradiation method. In this method, both, polymer and monomer are subjected to  $^{60}\text{Co}$  gamma rays at a dose of 11.85 kGy and 1.97 kGy/h dose rate. For the mentioned procedure, properly sealed ampoules were used. 400 mg of P(3HB) mixed with 1 mL of the monomer and 2 mL of solvent were added to the ampoules. The solvent effect on the final properties of the grafted polymers was studied. Typical solvents (S1, S2, S3, S4, S5 and S6) were used, and the results compared with the monomer free sample. The base polymer P(3HB) grafted with 2-aminoethyl methacrylate hydrochloride oligomer (AEMA) was purified by Soxhlet extraction using acetone solvent for five days. This procedure was carried out to eliminate the homopolymerization residues. Once purified, the material was dried under vacuum conditions to reach constant weight at 50–60 °C. All the polymer samples were kept for two weeks at room temperature to develop the full crystallization.

The sample's name is as follows: P1 refers to P(3HB) when it has reacted, or it is part of the molecule, while M1 is the AEMA monomer; for instance, P1M1S1 is the graft copolymer of P(3HB) with AEMA in ethanol media, and so on. Reproducibility was guaranteed by the four times repetition of the experiment in the same experimental conditions.

#### 2.2.2. Graft degree

The degree of grafting  $W$  (%) was obtained by gravimetric analyses of the mass increase of the graft copolymer relative to that of P(3HB), using the formula:

$$W\% = [(m_{\text{grafted polymer}} - m_{\text{P(3HB)}}) / m_{\text{P(3HB)}}] \times 100 \quad (1)$$

#### 2.2.3. Fourier-transform infrared spectroscopy

The sample films were prepared by solvent casting from  $\text{CHCl}_3$ . Thin films of about  $1 \text{ cm}^{-2}$  (area) and  $20 \mu\text{m}$  (thickness) was obtained and deposited on a support for FTIR investigation. The characterization of the resulting graft-copolymers film samples P (HB-g-M1) as well as the calculation of the crystallinity percentage was performed using the FTIR spectra. The infrared analysis was carried out in a Bruker Vector 33 spectrometer with a resolution of  $4 \text{ cm}^{-1}$  and 32 scans in transmission mode. In addition, the grafted polymer analysis was performed by Attenuated Total Reflectance (ATR) technique using a diamond crystal. 32 scans were necessary to obtain the final spectra of each sample, which was also collected with a  $4 \text{ cm}^{-1}$  spectral resolution.

#### 2.2.4. Dispersive Raman spectroscopic analysis

The characterization of the graft copolymers and the P(3HB) was obtained using a micro-Raman spectrometer (Bruker Senterra, model 910, MA, USA) equipped with a laser light source of 785 nm. The samples were analyzed with 10 s of integration time and 16 co-additions, a resolution  $9\text{--}15 \text{ cm}^{-1}$  and 100 mW. At the used excitation wavelength (785 nm), no fluorescent signal produced by grafted P(3HB) or blank was observed. The Raman shifts of the samples were measured from 200 to  $3100 \text{ cm}^{-1}$  in four intervals. The error in the band height determination is about 3–5% as usual. In order to avoid any interference between the support and the products' signals, the samples were placed on a flat and clean brass plate. Raman spectra of the polymers were obtained at room temperature in all cases.

#### 2.2.5. Nuclear magnetic resonance

Nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra were obtained on a Bruker Avance III HD 500 MHz operating at 500.15 MHz with a

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