



Synthesis and characterization of water-soluble chitosan grafted with hydrophilic aliphatic polyester



Jiajia Chen^{a,b}, Liuchun Zheng^{b,*}, Xiaonong Chen^{a,*}, Zhaodong Wang^b, Chuncheng Li^{b,*}, Yaonan Xiao^b, Guohu Guan^b, Wenxiang Zhu^b

^a Beijing Laboratory of Biomedical Materials, Beijing University of Chemical Technology, Beijing 100029, PR China

^b Beijing National Laboratory for Molecular Sciences, Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences (ICCAS), Beijing 100190, PR China

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ABSTRACT

Traditionally, hydrophobic aliphatic polyester has been employed to modify chitosan and organic soluble or swellable graft copolymers have been obtained. In this work, linear poly(butylene tartrate) (PBT) with hydrophilic pendant hydroxyl groups, which was synthesized by direct polycondensation of tartaric acid and butanediol under mild condition, was chosen to modify chitosan and synthesize PBT grafted chitosan (CS-g-PBT) with the mediation of 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide in aqueous solution of an ionic liquid. The chain length of the grafted PBT could be facilely controlled by varying the molecular weight of PBT. The chemical structures of CS-g-PBT were systematically characterized by ¹H NMR, attenuated total reflectance Fourier transform infrared and wide-angle X-ray diffraction. The thermal properties were investigated by thermogravimetric analysis and differential scanning calorimetry. The water solubility of chitosan has been effectively improved after grafting with PBT and a water-soluble chitosan derivative has been synthesized. Meanwhile, the water solubility of grafts varies regularly with chain length of grafted PBT.

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1. Introduction

Chitosan (CS), the fully or partially deacetylated derivative of chitin, is one of the abundant, renewable, biocompatible, biodegradable, and nontoxic carbohydrate polymers [1,2]. Therefore, CS has a variety of current and potential applications in pharmaceuticals [3], biotechnology [4], and food science [5]. However, due to the very strong intramolecular and intermolecular hydrogen bonds between hydroxyl groups and amino groups [6], CS has a major shortcoming of poor solubility. It is only soluble in acidic solution with pH <6, and insoluble in neutral and basic conditions as well as most organic conditions. Therefore, the application of CS is severely limited to acidic conditions.

Nowadays, aliphatic polyesters such as polylactide, polycaprolactone and poly(butylene succinate) have attracted considerable attention as useful materials because of the favorable biodegradability, biocompatibility and mechanical properties [7]. Grafting of aliphatic polyesters onto chitosan is a remarkable way to

obtain copolymer, which combines the merits of both chitosan and polyesters [8]. Most importantly, the CS can neutralize the acidic degradation products of polyesters due to its basic nature. Unfortunately, the aforementioned polyesters can only dissolve in organic solvents such as CHCl₃ and THF due to their hydrophobic nature. Consequently, the resulting graft copolymers are soluble or swellable in organic solvent, but insoluble in water, which is not environmentally friendly for the subsequent processing. Furthermore, grafting reactions usually take place in heterogeneous reaction medium and involve large quantity of volatile organic solvents. As a result, organic soluble chitosan intermediates, such as phthalochitosan, are also synthesized [9,10]. And this complicates the preparation process and increases the production cost.

Our working concept is to graft CS with water-soluble poly(butylene tartrate) (PBT), which has two pendant hydroxyl groups on every repeating unit, to improve the solubility of CS in water by a green process. It has been reported that aliphatic polyester with hydrophilic pendant hydroxyl groups can be useful in controlled drug delivery systems [11–13]. However, since pendant hydroxyl groups can take part in the polycondensation reaction resulting in branched and crosslinked structure, it is difficult to synthesize linear PBT. Therefore, the synthesis process always involves tedious protection and deprotection of the

* Corresponding authors. Tel.: +86 10 62562292; fax: +86 10 62562292.

E-mail addresses: hubeizlc@iccas.ac.cn (L. Zheng), chenxn@mail.buct.edu.cn (X. Chen), lichch@iccas.ac.cn (C. Li).

hydroxyl groups, and often causes degradation of the polymer backbone. Recently, it has been reported that linear polyesters with reactive pendant hydroxyl groups can be synthesized by one-step direct polycondensation under mild condition because of the low reactivity of pendant hydroxyl groups at a low temperature [14]. In this work, linear and water-soluble PBT were synthesized from L-tartaric acid (L-TA) and 1, 4-butanediol (BD) by this one-step strategy. The synthesized PBT was grafted onto CS via the coupling reaction between carboxyl groups on PBT chain and amino groups on CS mediated by 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC). To the best of our knowledge, this is the first example to modify chitosan with hydrophilic polyester. Just recently, ionic liquid (IL) was regarded as a new generation of green solvent, which is promising to replace the volatile organic compounds, owing to its low vapor pressure, excellent solubility and recyclability [15,16]. It has also been reported that some IL aqueous solutions can successfully dissolve chitosan [17]. In this research, the aqueous solution of the ionic liquid of 1-sulfobutyl-3-methylimidazolium trifluoromethanesulfonate (BSMIM-CF₃SO₃) was selected as a homogeneous and green reaction media for the coupling reaction. The resulting graft copolymers were systematically investigated by ¹H NMR, attenuated total reflectance Fourier transform infrared (ATR-FTIR), element analysis (EA), wide-angle X-ray diffraction (WARD), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and solubility.

2. Materials and methods

2.1. Materials

Chitosan (degree of deacetylation = 85%, determined by ¹H NMR analysis, $M_w = 52$ kDa) was supplied by Golden-shell Biochemical Corp. (Zhejiang, China). L-TA was purchased from Alfa Aesar (USA). BD and *p*-toluene sulfonic acid (PTSA) was obtained from Sinopharm Chemical Reagent Corp. (China). EDC was bought from Adamas (China). BSMIM-CF₃SO₃ was got from Shanghai Chengjie Chemical Corp. (China). All the other chemicals and solvents were of analytical grade and used as received without further purification.

2.2. Preparation of PBT

PBT was synthesized as follows: in a dry 250 mL four-neck round-bottom flask with mechanical stirring, 150 g of L-TA (1 mol), 88 mL of BD (1 mol) and 0.19 g of PTSA (1 mmol) were fed under nitrogen atmosphere. The temperature was raised to 80 °C. After the complete dissolution of L-TA in BD, the reaction system was gradually reduced to 4000 Pa and kept for 2 h. Then, the pressure was further reduced to 40–400 Pa and maintained for 5 h to complete the polycondensation reaction. The number-average molecular weight (M_n) of PBT was calculated from ¹H NMR spectrum according to the following equation:

$$M_n = 204 \times \frac{A_{4.25-4.28}}{A_{3.60-3.64}} + 120 \quad (1)$$

where $A_{4.25-4.75}$ and $A_{3.60-3.64}$ represented the integral areas of internal and terminal methylene protons of BD, 204 was the molecular mass of PBT repeating units and 120 was the average value of molecular mass of chain ends of L-TA and BD.

All the polyesters were purified by reprecipitation from their *N,N*-dimethyl formamide (DMF) solutions by ethyl acetate repeatedly, and dried for 12 h at 60 °C for further use.

2.3. Synthesis of CS-g-PBT

The CS-g-PBT was synthesized via the coupling reaction between carboxyl group of PBT and amino group of CS mediated by

EDC [18]. The synthetic procedure of CS-g-PBT was shown in Fig. 1. Typically, 0.2 g (1.2 mmol, calculated according to glucosamine units) of CS was dissolved in 20 mL of 2% (w/v) BSMIM-CF₃SO₃ aqueous solution. Then, predetermined amount of PBT (1.2 mmol) was added and stirred magnetically to obtain a homogenous solution. After that, predetermined amount of EDC (1.5 equivalent to PBT) was added and the pH was adjusted to 4.5–5 with BSMIM-CF₃SO₃. The reaction was maintained for 24 h under vigorous magnetic stirring at 25 °C. The product was dialyzed using dialysis membranes (MWCO 8 kDa) against distilled water for 3 days, and then lyophilized.

2.4. Elemental analysis

The contents of carbon, hydrogen and nitrogen in the products were measured with a FLASH EA1112 EA. The grafting content of PBT in the copolymer was calculated according to Eq. (2) [19].

$$N_{CS}/(1+x) = N_{CS-g-PBT} \quad (2)$$

where N_{CS} and $N_{CS-g-PBT}$ were the contents of the nitrogen element in CS and CS-g-PBT respectively; and x was weight percentage of PBT relative to CS, which represented the grafting content of PBT.

2.5. ATR-FTIR spectroscopy

ATR-FTIR spectra were recorded with a Nicolet 6700 FTIR equipped with attenuated total reflectance device (Smart Orbit) from 650 to 4000 cm⁻¹ at room temperature. The samples were scanned 32 times and the resolution ratio was 4 cm⁻¹.

2.6. NMR spectroscopy

¹H NMR spectra were performed on a Bruker DMX-400 NMR spectrometer using D₂O/CF₃COOD (95:5, v/v) as solvent for CS, and D₂O for the rest samples.

2.7. Wide-angle X-ray diffraction (WAXD) analysis

WAXD measurements were conducted with a Ragaku Model D/max-2B X-ray diffractometer (Japan) with a Cu/k α radiation (40 kV, 20 mA), and the experimental data were recorded in the range of 3–60° at a scanning rate of 2° min⁻¹.

2.8. Thermal analysis

DSC analysis was carried out with a TA Q2000 differential scanning calorimeter (TA Instruments) at a scanning rate of 20 °C min⁻¹ under nitrogen atmosphere (50 mL min⁻¹). The samples were first heated to 180 °C and maintained for 5 min to eliminate thermal histories. After that, they were cooled to 0 °C and held for 10 min. Finally, the samples were reheated again to 180 °C. Both the cooling and heating scans were recorded for analysis.

TGA was performed on Perkin-Elmer TGA-7. Samples were heated from 50 °C to 600 °C at a rate of 20 °C min⁻¹ under nitrogen atmosphere.

2.9. Solubility test

0.1 g of CS-g-PBT was dispersed in 1 mL of distilled water or 1% (w/v) acetic acid aqueous solution and stirred at 60 °C for 6 h. High temperature has also been endowed to do the water solubility tests by other researchers to improve the dissolution rate and save time [20–22]. The samples were then centrifuged at 10,000 rpm for 10 min. The transparent solution was carefully pipetted out without disturbing the precipitated sample concentrated at the

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