

Short communication

Synthesis of starch-g-lactic acid copolymer with high grafting degree catalyzed by ammonia water



Yingmo Hu*, Mingru Tang

School of Materials Science and Technology, China University of Geosciences, Beijing 100083, China

ARTICLE INFO

Article history:

Received 19 January 2014

Received in revised form 20 October 2014

Accepted 10 November 2014

Available online 18 November 2014

Keywords:

Starch

Lactic acid

Ammonia water

Graft copolymer

Degradable

ABSTRACT

The study of starch-g-lactic acid copolymer has gained much attention for its completely degradable property, but its intricate synthetic procedure and low graft degree inhibited its further application. In this work, the synthesis of starch-g-lactic acid copolymer was attempted via the catalysis of ammonia water by one-step process, and the structure of starch-g-lactic acid copolymer was characterized by means of IR, ^{13}C NMR and HMBC. The synthetic conditions were optimized as follows, the starch was activated for 2 h at 80 °C at first, starch and lactic acid with weight ratios of 1:4 reacted for 4 h at 90 °C in vacuum. The starch-g-lactic acid copolymer can be finally obtained with graft degree of starch 58.9%.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Recently, the copolymer of starch graft with lactic acid has been explored widely owing to the excellent degradability of both starch and poly(lactic acid). Therefore, the starch-g-lactic acid copolymer has been synthesized by diverse procedures such as ring-opening polymerization of lactide with catalysis of stannous 2-ethyl-hexanoate (Xie, Shi, Xie, & Zhou, 2006), initiation by potassium tert-butoxide (You, Shen, Jiao, Li, & Zhu, 2002), or introducing some protective groups and substituent groups into raw materials and then to react (Dubois, Krishnan, & Narayan, 1999). Wang, Hu and Zhu (2012) prepared starch-g-lactic acid copolymer directly via the reaction of cornstarch with lactic acid catalyzed by sodium hydroxide with a grafting degree of 33.6%. However, either the procedures are very complex, or the grafting degree is too low. Thus, the synthetic method of starch-g-lactic acid copolymer needs to be further investigated to get more suitable condition and high grafting degree.

In this work, a new synthetic system was investigated in which the starch graft copolymerized with lactic acid was directly catalyzed by ammonia water under gentle condition in order to produce starch-g-lactic acid copolymer with high graft degree. The structure of starch-g-lactic acid copolymer was also characterized by means of IR, ^{13}C NMR and HMBC.

2. Experimental

2.1. Materials and equipments

Corn starch was obtained from Beijing Gusong Economics & Trade Co. Ltd. Ammonia water (A.R), Urea (A.R), ethanol (A.R) and acetone (A.R) were purchased from Beijing Chemical Works. Lactic acid (A.R) was obtained from Xilong Chemical Company.

Corn starch and graft copolymer were characterized by IR (Perkin-Elmer 100) in the wavelength range from 4000 to 450 cm^{-1} , XRD (D/max-Ra diffractometer) with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) operating at 40 kV and 100 mA in the range of 3–35° of 2θ by steps of 0.02°, ^{13}C NMR and HMBC (Bruker AV-600) with d_6 -DMSO as solvent, and SEM (JEOL, JSM-7001F with resolution at 10 μm , 5.0 kV), respectively.

2.2. Synthesis of starch-g-lactic acid copolymer

The 30 mL urea solution, 15 mL $\text{NH}_3 \cdot \text{H}_2\text{O}$ (25%) and 5.00 g starch were added into the flask and stirred adequately at 80 °C for 2 h. Then lactic acid was added into the flask to react under vacuum at 90 °C for 4 h, and the mixture was precipitated by ethanol to remove excessive lactic acid and residual solvent after cooling to room temperature. Then it was dried to get crude product. And then the crude product was purified with soxhlet extraction at 80 °C for

* Corresponding author. Tel.: +86 1082322759; fax: +86 1082322974.
E-mail address: huyingmo@163.com (Y. Hu).

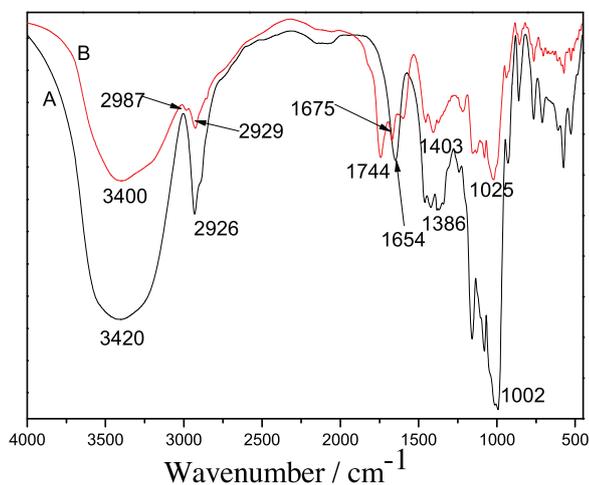


Fig. 1. IR spectra of starch (A) and starch-g-lactic acid copolymer (B).

40 h to obtain the final starch-g-lactic acid copolymer. The grafting degrees were calculated with the following formula:

$$\text{grafting degree} = \frac{m_1 - m_0}{m_0}, \quad (1)$$

where m_0 is the weight of raw corn starch, and the m_1 is the weight of the final copolymer product.

3. Results and discussion

3.1. Characterizations of starch-g-lactic acid copolymer

3.1.1. IR spectra of starch-g-lactic acid copolymer

The IR spectra of starch and starch-g-lactic acid copolymer were shown in Fig. 1. The broad and strong absorption peak in the 3252–3547 cm^{-1} region is attributed to the stretching vibration of $-\text{OH}$, and the peaks at 2929 cm^{-1} , 1654 cm^{-1} , and 1161–1002 cm^{-1} are assigned to the vibrational absorption of C–H bond, intramolecular hydrogen bond and C–O bond in starch respectively (Curve A). Compared to IR spectrum of starch, the IR spectrum of starch-g-lactic acid copolymer (Curve B) displayed two new absorption peaks, which are the characteristic absorption of carbonyl group stretching at 1744 cm^{-1} and the stretching vibration of C–H bond in poly(lactic acid) chain at 2987 cm^{-1} , respectively. The other absorption peaks all correspond to those of starch except that some peaks shift for a few wavenumbers owing to electric effects of ester group, which indicated that the starch-g-lactic acid copolymer was synthesized in this system.

3.1.2. ^{13}C NMR spectra analysis

The ^{13}C NMR spectra of starch and starch-g-lactic acid copolymer were shown in Fig. 2. It was found from the ^{13}C NMR spectra of starch (Fig. 2A) that the chemical shift of the peak at $\delta 100$ ppm and $\delta 79$ ppm were assigned to carbons C_2 , C_3 and C_6 attached to $-\text{OH}$ of the starch unit respectively. The signal in the $\delta 71$ –72 ppm region is attributed to C_1 , C_4 and the carbon C_5 attached to CH_2 occurred at $\delta 60$ ppm. Compared to the peaks of starch (Fig. 2A), Fig. 2B showed extra peaks belonging to long chain of poly(lactic acid). The methyl carbon at $\delta 21$ ppm, carbon of CH_2 and CH in the region of $\delta 66$ –72 ppm and obvious carbonyl carbon peak at $\delta 177$ ppm in the ester, all corresponded with the typical structure of starch-g-lactic acid copolymer.

3.1.3. Heteronuclear Multiple Bond Coherence (HMBC) analysis

Fig. 3 displays the HMBC spectra of starch and starch-g-lactic acid copolymer. As for the HMBC spectra, the ^{13}C spectrum was

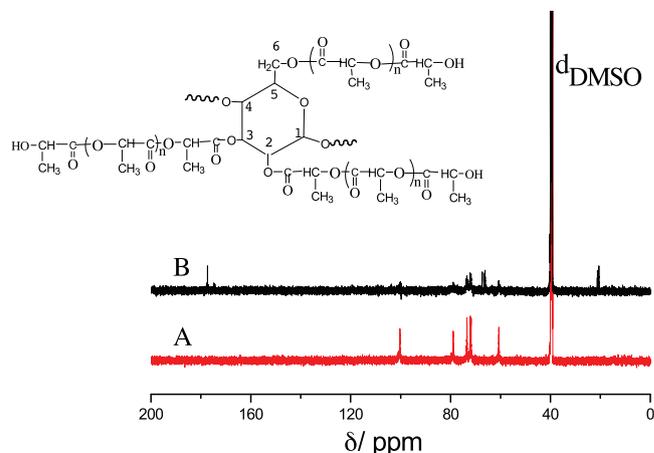


Fig. 2. ^{13}C NMR spectra of corn starch (A) and starch-g-lactic acid copolymer (B).

presented along the vertical axis and the ^1H spectrum was shown along the horizontal axis. It is obvious that hydrogens are attached to carbons for cross peaks relating the two types of spectra in the field, and the cross peak of the ^{13}C peak at 40 ppm and the ^1H peak at 2.5 ppm are attributed to the methyl of DMSO as shown in Fig. 3. The blue arrow was taken from singlet of the peak at 54 ppm out to the correlation peak in the x - y field and dropped down to the horizontal axis at 3.6 ppm, which correspond to the signals of C_2 and C_3 in starch ring and related to the vertical axis at 40 ppm produced by C_6 in starch. The ^1H NMR shows that the signal at 2.6 ppm was caused by the hydrogen on the CH group which was related

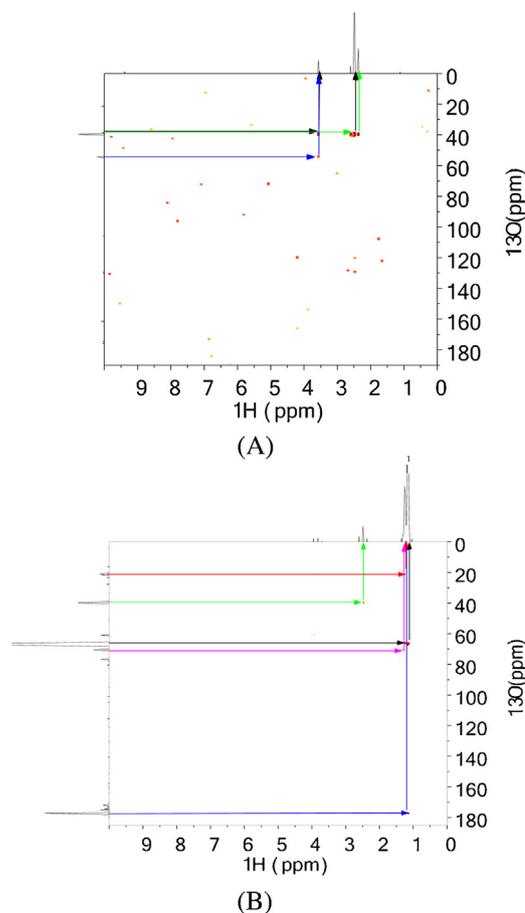


Fig. 3. HMBC spectra of starch (A) and starch-g-lactic acid copolymer (B).

Download English Version:

<https://daneshyari.com/en/article/1383839>

Download Persian Version:

<https://daneshyari.com/article/1383839>

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