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Synthesis of cationic starch with a high degree of substitution in an ionic liquid

Yingbin Wang, Wenlei Xie *

School of Chemistry and Chemical Engineering, Henan University of Technology, Zhengzhou 450052, PR China

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ABSTRACT

Cationic corn starch derivatives containing quaternary ammonium groups with a high degree of substitution were synthesized by reacting corn starch with glycidyltrimethylammonium chloride (GTAC) in a homogeneous manner using 1-butyl-3-methylimidazolium chloride (BMIMCl) as a reaction medium. The influence of reaction time, reaction temperature, the amount of catalyst NaOH and molar ratio of GTAC/anhydroglucose units in starch on the degree of substitution (DS) of products was investigated. The maximum DS value obtained in the optimum reaction condition was up to 0.99. Furthermore, the structure of cationic starch derivatives was characterized by means of Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), X-ray powder diffraction (XRD), thermal analysis and ^{1}H NMR spectroscopy. The results showed that the ordered crystalline structure of native starch was largely destroyed during the dissolution and functionalization of starch in the ionic liquid BMIMCl, leading to an uniform etherification reaction to be carried out under the homogeneous reaction conditions.

1. Introduction

Starch has attracted much attention for industrial use in recent years because of its relative low price, renewability and biodegradability. However, the utilization of native starch is limited by its physicochemical properties such as water insolubility and its tendency to form unstable pastes and gels. Therefore, starch is usually modified physically or chemically to improve its functionality for industrial applications and thus to extend its usefulness. As one of the chemically modified starches, cationic starches are widely used as additives, for example in the paper, textile, wastewater treatment and related industry. The properties of cationic starch derivatives, such as thermoplasticity and water dissolution, are highly dependent on the preparation method used, the type of cationic groups and the degree of substitution (DS). At present, cationic starches with a high-DS are of increasing interest owing to the promising candidate to replace the synthetic flocculating agents in diverse industrial applications (Bendoraitiene, Klimaviciute, Sableviciene, & Zemaitaitis, 2005; Haack, Heinze, Kulicke, & Oelmeyer, 2002; Krentz et al., 2006).

Conventionally, the high-DS cationic starch can be prepared by the etherifying reaction of starch with the tertiary amino and quaternary ammonium cationizing reagents, such as glycidyltrimethylammonium chloride (GTAC) or 3-chloro-2-hydroxypropyltrimethylammonium chloride (CTAC) in heterogeneous or homogeneous reaction conditions. It was reported that starch was effectively cationized using GTAC or CTAC in an aqueous alcoholic solvent, since the addition of alcohol to the alkaline aqueous media could result in the high-DS cationic starch (Han & Sosulski, 1999; Kweon, Sosulski, & Bhirud, 2006). When starch was modified with CTAC in ethanol/water suspension, the DS value of cationic starch was affected by the substrate ratio and varied between 0.03 and 0.88. Furthermore, the process of the starch modification with GTAC in aqueous sodium hydroxide heterogeneously or in dimethylsulfoxide (DMSO) homogeneously was more effective than in ethanol/water media (Heinze, Haack, & Rensing, 2004). Additionally, Wang and co-workers (Wang et al., 2009) prepared high-DS cationic corn starch in different organic media and obtained the cationic starch with a DS value of 1.37 in dioxane–THF–water media. However, in the aforementioned process a large amount of sodium hydroxide solution or toxic solvent has to be used and serious environmental pollution may be caused.

More recently, room-temperature ionic liquids (ILs), which are considered as desirable green solvents for a wide range of separation and as reaction media, have received significant attention (Welton, 1999). Moreover, the room-temperature ILs having the imidazolium structure have been found to be nonderivatizing solvents for polysaccharides, such as starch (Seoud, Koschella, Fidale, Dorn, & Heinze, 2007). In ILs, namely 1-butyl-3-methylimidazolium chloride (BMIMCl), starch could be dissolved up to 15% (wt/wt) concentration at 80 °C (Stevenson, Biswas, Jane, & Inglett, 2007). By using BMIMCl as a reaction medium, the acetylation of starch could be conducted with a mixture of acetic anhydride and pyridine in a homogeneous manner, yielding the starch acetate with 0.3–2.6 DS (Biswas, Shogren, Stevenson, Willett, & Bhowmik,

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* Corresponding author. Tel.: +86 371 67756302; fax: +86 371 67756718.
E-mail address: xwenlei@163.com (W. Xie).

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2006). Besides, the synthesis of polymer-grafted starch in BMIMCl was also reported in the literature (Xu, Wang, & Liu, 2008).

In the present investigation, cationic corn starches with a high-DS were prepared homogeneously by the reaction of native corn starch with GTAC in BMIMCl reaction medium. The major factors affecting the cationization reaction, such as the molar ratio of GTAC/anhydroglucose units (AGU) in starch, reaction time, the amount of catalyst NaOH and reaction temperature were investigated. Further, starch derivatives obtained were characterized by Fourier transform infrared (FT-IR) spectroscopy, X-ray diffractrometry (XRD), scanning electron microscopy (SEM), thermal analysis and ^{1}H NMR spectroscopy.

2. Materials and methods

2.1. Materials

Corn starch, which contained 25% amylose and 75% amylopectin, was obtained from Linghua Company (Jining, China) and dried at 80 °C for 24 h before use. The cationic etherifying agent, glycidyltrimethylammonium chloride (GTAC) was synthesized according to the literature (Yang & Guo, 2007). 1-Methylimidazole and 1-chlorobutane were obtained from Aldrich Chemical Company. All other chemicals were of analytical grade and used as received without further purification.

2.2. Preparation of ionic liquid BMIMCl

Ionic liquid BMIMCl was synthesized according to the procedures described elsewhere (Huddleston et al., 2001). Equal molar amounts of chlorobutane and 1-methylimidazole were added into a three-necked flask fitted with a reflux condenser and a mechanical stirrer. The reaction was carried out at 70 °C for 24–72 h under stirring until two phases were formed. The top phase, containing unreacted starting material, was decanted and ethyl acetate (a volume approximately equal to half of that of the bottom phase) was added with thorough mixing. Subsequently, the ethyl acetate was decanted followed by the addition of fresh ethyl acetate and this procedure was repeated twice. After the third decanting of ethyl acetate, any remaining ethyl acetate was removed by heating the bottom phase to 70 °C under reduced pressure. The obtained product, BMIMCl, was a slightly yellow viscous ionic liquid and may be crystalline at room temperature. Mp: 66–67 °C. The ^{1}H NMR (D_2O, ppm) spectrum of BMIMCl shows the following peak locations: δ 0.92 (3H,t), 1.35 (2H,m), 1.78 (2H,quintent), 3.71 (3H,s), 4.08 (2H,t), 7.06 (1H,s), 7.18 (1H,s) and 7.63 (1H,s). The C NMR spectrum (ppm) contains peaks at: δ 15.21, 33.561, 35.73, 38.12, 51.86, 121.34, 127.29 and 143.54. The H/C NMR spectra were consistent with the results reported by Huddleston et al. (2001).

2.3. Synthesis of cationic corn starches

In a three-neck round flask equipped with a magnetic stirrer, dried corn starch was added to the prepared BMIMCl at a concentration of 10% (w/w). The mixture solution was stirred thoroughly at 80 °C until the starch was dissolved completely. To this mixture, the cationization reagent GTAC and the requisite amount of aqueous NaOH solution were added at a certain temperature, respectively. After stirring for the required time, the reaction mixture was cooled to room temperature and then isolated by precipitation in absolute ethanol with stirring. The obtained precipitate was collected and washed thoroughly with ethanol to eliminate BMIMCl, unreacted GTAC and by-products. Finally, the product was dried at 50 °C in vacuum oven for 48 h.

The nitrogen content of cationic starches was determined by the Kjeldahl method using a KDN-08C Kjeldahl instrument (Shanghai Hongji Corporation, China). The samples were analyzed in triplicates and the degree of substitution (DS) was calculated according to the following equation (Kavaliauskaite, Klimaviciute, & Zemaitaitis, 2008).

$$\mathrm{DS} = 162\mathrm{N}/(1400 - 151.5 \times \mathrm{N})$$

where N is nitrogen content determined by the Kjeldahl method, %, 162 is the molecular weight of AGU, and 151.5 is the molecular weight of GTAC.

2.4. Characterizations of cationic starch

FT-IR spectra of native and cationic starch were recorded on a Shimadzu IR-Prestige-21 spectrometer (Shimadzu Corporation, Japan) using KBr disc technique. For FT-IR measurement, the samples were mixed with anhydrous KBr and were then compressed into thin disk-shaped pellets. The spectra were obtained with a resolution of 4 cm^{-1} between a wave number range of 400 and 4000 cm^{-1}.

X-ray powder diffraction measurements were conducted on a D8 FOCUS X-ray diffractometer (Bruker AXS Corporation, Germany) operating at 35 mA and 40 kV. The X-ray source was Cu $K\alpha$ filtered radiation (λ = 0.15418 nm). The scattering angle (2θ) was varied from 5° to 40° with a step width of 0.02°.

SEM images were obtained with a JSM-6700F scanning electron microscope (JEOL). The samples were mounted on an aluminum stub with a double sticky tape, followed coating with the gold in a vacuum before examination.

The thermal analysis of native starch and cationic starch was carried out using NETZSCH STA409PC thermal analyzer. TG and DTG analyses were performed with a heating rate of 10 °C/min between temperature ranges of room temperature to 600 °C in an atmosphere of flowing dry nitrogen.

^{1}H NMR spectra were acquired on a Bruker AV 300 MHz spectrometer (Bruker Corporation, Switzerland) operating at 500.13 MHz. Samples were dissolved in DMSO-d6 using tetramethylsilane as internal standard. The chemical shifts were expressed in ppm.

3. Results and discussion

3.1. Influence of the reaction parameters

In general, the limited solubility of biopolymers restricts the nature of reagents that could have been used to modify these biopolymers. In this investigation, corn starches were cationically modified using GTAC in BMIMCl. BMIMCl can efficiently dissolve starches and provide feasible reaction environments for the functionalization and therefore a homogeneous etherification reaction could be achieved in this IL. The homogeneous modification of starch relies upon the destructurisation of the semi-crystalline starch granules and the effective dispersion of starch, allowing starch hydroxyl groups more accessible to electrophilic reactants. During the modification of starch in this study, several factors could influence the extent of the starch cationization. These factors include the sodium hydroxide concentration, GTAC/AGU molar ratio, reaction time and reaction temperature. The optimization of cationization process was performed by varying the reaction parameter while other parameters were kept constant.

The influence of various molar ratios of NaOH to starch (AGU) on the DS value is presented in Fig. 1. As observed, without addition of NaOH in the reaction mixture, the product obtained had a DS value of 0.021, and the initial increase in the molar ratio of NaOH/AGU favorably increased the DS value until the DS value