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Modification of hydroxypropyl guar gum with ethanolamine

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ABSTRACT

A new guar gum derivative containing amino group was synthesized through nucleophilic substitution of p-toluenesulfonate activated hydroxypropyl guar gum with ethanolamine. For the preparation of p-toluenesulfonate esters hydroxypropyl guar gum, the results showed that the reaction rate was optimal at 25 °C and the reaction could reach equilibrium state when it was carried out for 10 h at 25 °C. For the nucleophilic substitution of tosyl group with ethanolamine, the reaction was completed after 10 h reaction at 50 °C. The structures of products were characterized by NMR and FT-IR spectroscopy. The results showed that the p-toluenesulfonate esters can be effectively substituted by ethanolamine to form the hydroxyethyl amino hydroxypropyl guar gum (EAHPG). The content of nitrogen of EAHPG was determined by acid–base titration and element analysis.

1. Introduction

Natural or modified polysaccharides containing amino group, which show good biological and metal ion absorption properties, are explored intensively as materials for bio-related applications and water treatment. Chitin and chitosan composed of N-acetylglucosamine and glucosamine residues have been widely used in pharmaceutical, cosmetics, biomedical, biotechnological, agricultural, food, and non-food industries as well (water treatment, paper, and textile) (Ravi Kumar Majeti, 2000). β-Glucan derivative modified by amino group shows higher bile acid binding activity than native β-glucan. The aminated β-glucan derivative also shows pronounced antimicrobial effects against *Escherichia coli* and *Bacillus subtilis*, and ACE (angiotensin-converting enzyme) inhibition activities (Shin, Lee, Lee, & Lee, 2005). Starch derivatives modified by amino group were used to absorb the metal ion in water (Dong et al., 2010; Xie, Shang, Liu, Hu, & Liao, 2011).

Guar gum (GG) is a non-ionic, water-soluble, biodegradable and biocompatible hetero polysaccharide composed of a β-(1-4) D-mannopyranose backbone linked with α-(1-6) D-galactopyranose units (Reuben, 1985). Modification of guar gum with amino group may bring guar gum new functionalities and enlarge its application. Some guar gum derivatives modified by amino polymers and alkyl amine have been synthesized and found interesting applications in drug controlled release system, antibacterial material and protein partition (Bahamdan & Daly, 2007; Das, Ara, Dutta, & Mukherjee, 2011; Kautharapu et al., 2009; Soppirnath & Aminabhavi, 2002).

In this work, a new guar gum derivative containing amino group was synthesized through nucleophilic substitution of p-toluenesulfonate activated hydroxypropyl guar gum (HPG) with ethanolamine, which has not been reported previously in our knowledge. The reactions were systematically studied. The structure of products was characterized by NMR and FI-IR. The content of nitrogen of EAHPG was determined by acid–base titration and element analysis.

2. Experimental

2.1. Materials

The hydroxypropyl guar gum (HPG, MS = 1.7, Mw = 7.8×10^4 g/mol) was kindly provided by the Jingkun Oilfield Chemistry Company, Jiangsu in China. Pyridine, acetone, ethanolamine, sodium hydroxide, p-toluene sulfonyl chloride, are all analytical grade regents and used without further purification.

2.2. Synthesis of p-toluenesulfonate esters HPG (HPG-Tos)

Four grams HPG was dissolved in 30 ml pyridine at 7 °C with stirring for a moment, then a solution of 6 g p-toluene sulfonyl chloride dissolved in 30 ml pyridine was added dropwise to the reaction mixture over a period of 0.5 h. After this, the reaction temperature was raised to 25 °C and continued for 10 h. The resultant HPG-Tos was thereafter precipitated by pouring the reaction mixture into abundant ethanol. For purification, the crude products were dissolved in a suitable quantity of acetone, and separated by adding abundant ethanol to the solution. In accordance with this method,

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the products were purified for three times. Finally the HPG-Tos was vacuum freeze-dried for 48 h.

2.3. Preparation of hydroxyethyl amino hydroxypropyl guar gum (EAHPG)

Four grams HPG-Tos was added into 20 ml ethanolamine under stirring. The reaction temperature was gradually increased to 50 °C and continued for 10 h. The substituted HPG was isolated from the reaction solution by adding abundant acetone. To further purify the EAHPG, the crude EAHPG was dissolved in suitable quantity of deionized water, and the obtained water solution was then dropwise added into abundant acetone to give flocculent products. This purification process was repeated for three times. Finally, the EAHPG was vacuum freeze-dried for 48 h.

2.4. FT-IR spectra

The IR spectra were obtained from samples in KBr pellets using a BRUKER TENSOR spectrophotometer.

2.5. ^{13}C and ^{1}H NMR spectra

HPG-Tos was dissolved in d_6-acetone for ^{13}C NMR spectra analysis, and hydrolyzed by 10% DCl for ^{1}H NMR spectra analysis. Both HPG and EAHPG were dissolved in 10% DCl water solution for ^{13}C NMR spectra analysis. All NMR spectra of samples were recorded at 298 K on a Bruker Avance III 600 MHz NMR spectrometer.

2.6. Determination of the degree of substitution (DS) of esters in HPG-OTs and the DS of amino group in EAHPG

2.6.1. Determination of DS of tosyl group

^{1}H NMR spectra of HPG-OTs hydrolyzed by 10% DCl was used to calculate the DS of Tosyl group in HPG-Tos (DS_{Tos}) with the following formula:

$$DS_{Tos} = \frac{\text{integral (phenyl-H)}}{4 \times \text{integral}\,(\text{G-H}_1 + \text{M-H}_1)} \quad (1)$$

where integral (phenyl-H) is the peak area of phenyl of tosyl group whose peaks shows at 7.4 ppm and 7.7 ppm, integral ($G\text{-}H_1 + M\text{-}H_1$) is the peak area of H-1 of galactosyl and mannosyl whose peaks show at 4.5–5.5 ppm (Wu et al., 2010).

2.6.2. Determination of the DS of amino group in EAHPG

In this work, the content of nitrogen measured by element analysis and acid–base titration was used to determine the DS of amino group.

The process of acid–base titration was as follows: 0.2 g of EAHPG was dissolved in 20 ml 1 mol l^{-1} HCl and hydrolyzed for 0.5 h at 80 °C. Then the pH of resultant solution was adjusted to 2.2 with 1 mol l^{-1} NaOH, after which the solution was titrated by 0.0256 mol l^{-1} NaOH. Each sample was analyzed three times under the same conditions and the average value was used.

3. Results and discussion

p-Toluenesulfonate ester is easily formed by reaction of hydroxyl group with p-toluene sulfonyl chloride and displaced by other group with nucleophilicity. p-Toluenesulfonate ester was widely chosen as intermediate to modified compound with hydroxyl group.

In this study, HPG-Tos was firstly synthesized by esterification of HPG with p-toluenesulfonyl chloride in pyridine. Then the tosyl group of HPG-Tos was substituted by ethanolamine to form the EAHPG.

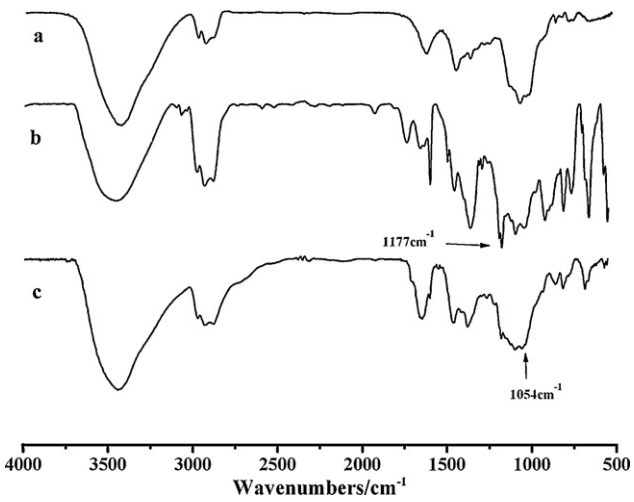

Fig. 1. FT-IR spectrum of HPG (a), HPG-Tos (b) and EAHPG (c).

3.1. Analysis of FT-IR spectra

Fig. 1 shows the FT-IR spectra of HPG, HPG-OTs and EAHPG. The spectrum of HPG displays the O—H stretching absorption at 3400 cm^{-1}, the C—H stretching absorption at 2971 cm^{-1}, 2920 cm^{-1}, and the C—O—C stretching at 1080 cm^{-1}. For HPG-OTs, the absorption band at 1177 cm^{-1} is assigned to the —S=O stretching vibration (Tiller, Berlin, & Klemm, 1999) and the bands at 1600 cm^{-1}, 1500 cm^{-1} and 1450 cm^{-1} correspond to the stretching vibration of aromatic groups. After reaction of HPG-Tos with ethanolamine, the absorption band at 1177 cm^{-1} assigned to —S=O stretching vibration almost disappears and the strength of absorption band at 1504 cm^{-1} assigning to primary hydroxyl group increases, indicating that the tosyl group is displaced by ethanolamine.

3.2. Analysis of ^{13}C NMR spectra

Fig. 2 shows the ^{13}C NMR spectrum of the HPG-OTs in d_6-acetone. The resonance at 18.3 ppm was assigned to the native methyl groups of hydroxypropyl (Ding et al., 2008), the resonance at 16.95 ppm was attributable to methyl groups of hydroxypropyl modified by p-toluenesulfonate ester, and the resonance at 20.84 ppm corresponds to the methyl groups of tosylate. The chemical shift from 127 ppm to 145 ppm was assigned to the backbone of aromatics of benzoate and tosylate (Tiller et al., 1999). The carbon signals of galactosyl, mannosyl and methine of hydroxypropyl between 58 ppm and 69 ppm (Ding et al., 2008) are overlaped and therefore, it is hard to find valuable information from this region.

^{13}C NMR spectra of EAHPG and native HPG dissolved in 10% DCl were shown in Fig. 3. The occurrence of new resonances at 45.8 ppm and 53.3 ppm were assigned to the methylene carbons of hydroxyethyl amino groups (—NH—$\mathbf{C}H_2$—$\mathbf{C}H_2$—OH) (Bonnet, Boyer, Langlois, Duval, & Rabiller, 2003), and the resonance at 56.3 ppm was attributable to the methine carbons of hydroxypropyl modified by amino groups, while the signal at 12.6 ppm was attributable to the methyl carbons of hydroxypropyl modified by amino groups (Sieval et al., 1998). The resonance at 49.2 ppm can be assigned to the C-6 (—$\mathbf{C}H_2$—NH—CH_2—CH_2—OH) modified by amino groups in glycosyl (Berlin, Klemm, Tiller, & Rieseler, 2000). The resonance at 20.5 ppm corresponds to the methyl groups of residual tosylate. The appearance of new resonances at 12.6 ppm, 45.8 ppm, 49.2 ppm, 53.3 ppm and 56.3 ppm indicated the HPG was successfully modified by ethanolamine.

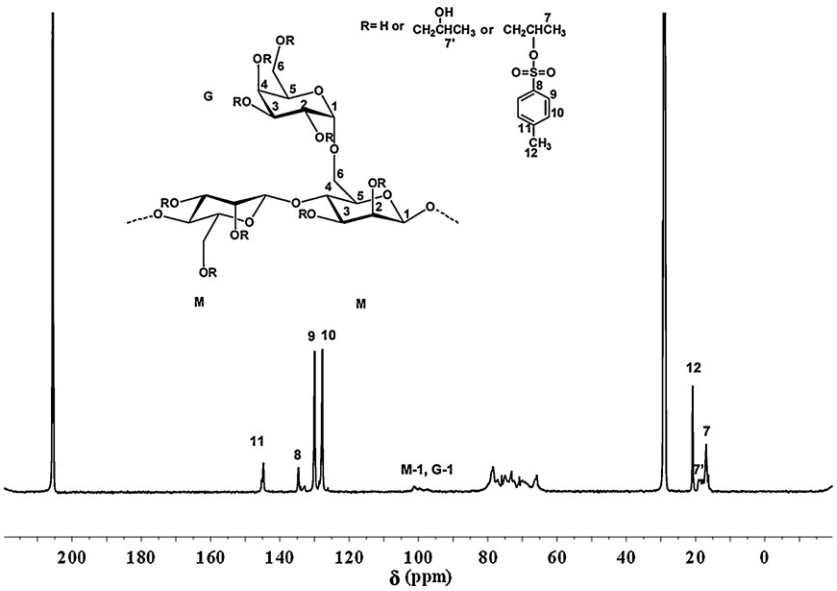

Fig. 2. ^{13}C NMR spectrum of HPG-Tos with DS_{Tos} of 1.16.

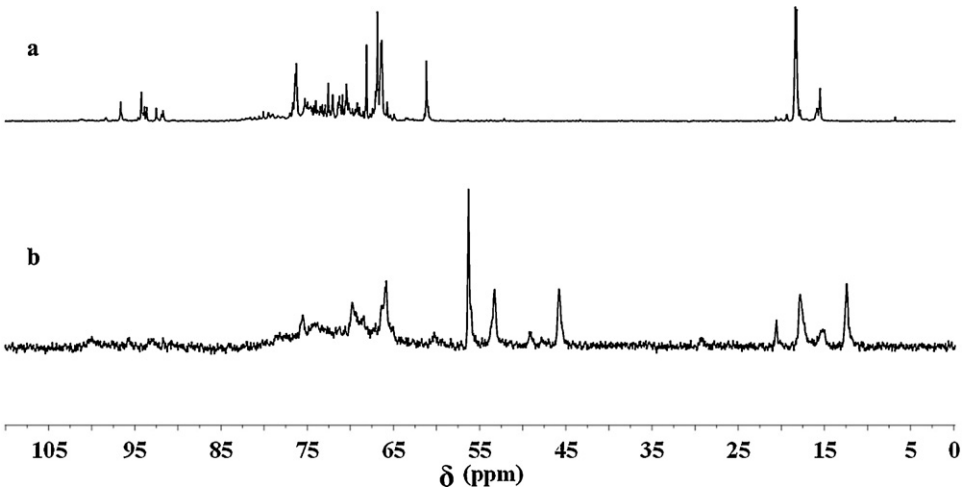

Fig. 3. ^{13}C NMR spectra of HPG (a) and EAHPG (b).

3.3. Determination of the DS of amino group in EAHPG

The potentiometric titration in excess of HCl gave two well-defined transitions and peaks in the integral and differential titration curves, respectively. The first peak in differential titration curves correspond to titration of the excess of HCl. The second peak corresponds to titration of —NH—. Fig. 4 gives a pH-titration curve of EAHPG. The content of nitrogen ($Wt_{(N)}$) could be calculated through the consumption of sodium hydroxide with Eq. (2):

$$Wt_{(N)} = \left\{ \frac{[M_{(N)} C_{NaOH}(V_2 - V_1)]}{m} \right\} \times 100 \quad (2)$$

where m was the mass of EAHPG using in titration experiments, $M_{(N)}$ was the relative atomic mass of nitrogen, V_1 was the volume consumption of sodium hydroxide at the first transition of the titration curve, which represented the neutralization of HCl in excess, V_2 was the volume consumption of sodium hydroxide at the second transition of the titration curve. $V_2 - V_1$ represented the neutralization of —NH_2^+— groups, and the [C_{NaOH} ($V_2 - V_1$)] represented the mol value of the —NH— groups.

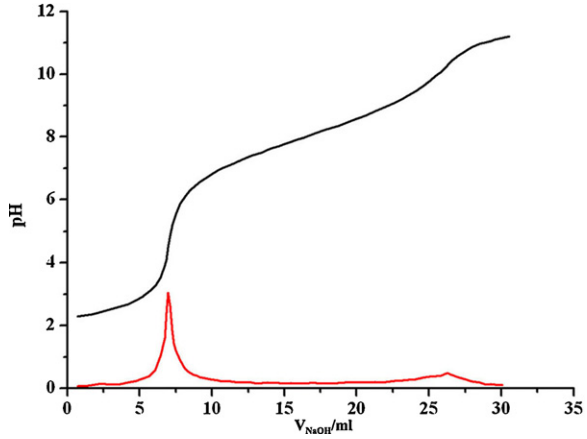

Fig. 4. The curve of titration of EAHPG (red curve was the differential of the black curve). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

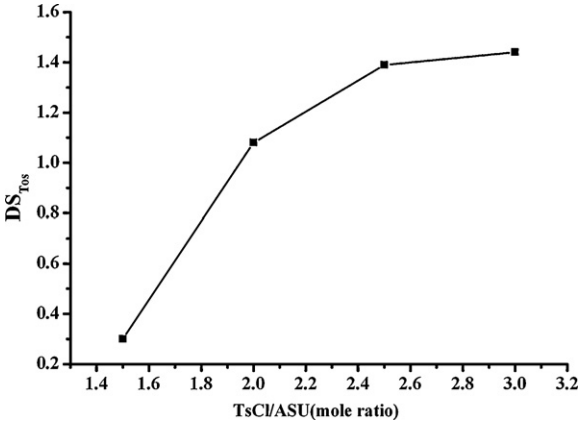

Fig. 5. The trend of DS_{Tos} along with the increase of monomer ratio.

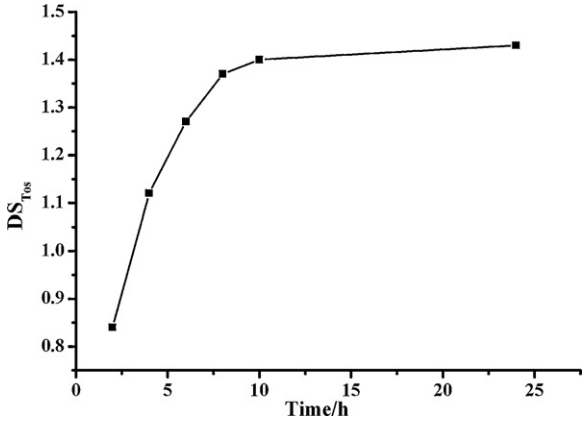

Fig. 7. Effect of reaction time on DS_{Tos}. (The mole ratio of TsCl:ASU is 1:2.5, and the reaction temperature is 25 °C.)

3.4. Effect of reaction conditions on the preparation of HPG-Tos

3.4.1. Effect of the monomer ratio on the DS_{Tos}

In order to investigate the variation of DS_{Tos} along with the mole ratio of primary materials, a series of reactions were carried out at 25 °C for 10 h with mole ratio of TsCl to a sugar unit in HPG (ASU) increasing from 1.5:1 to 3:1. The effect of mole ratio of TsCl to the ASU on the DS_{Tos} was shown in Fig. 5. The DS_{Tos} increased with the increasing concentration of TsCl, and leveled off at about the mole ratio of TsCl to ASU = 2.5. There are three different kinds of hydroxyl groups in HPG which possess different tosylation reactivity. The hydroxyl groups of hydroxypropyl can be substituted more easily by the tosyl groups than other hydroxyl groups in HPG. As shown in Fig. 5, the maximum DS_{Tos} value is about 1.44, which is in accordance with the DS value of hydroxyl group of hydroxypropyl in HPG as we previously reported (Ding et al., 2008; Wu et al., 2010). This may also indicates that the tosylation reaction occurs mostly at hydroxyl groups of hydroxypropyl in HPG.

3.4.2. Effect of reaction temperature on the DS_{Tos}

A series of reactions at different temperature were carried out to investigate the effect of reaction temperature on the DS_{Tos}. Fig. 6 shows variations in the DS_{Tos} as a function of the reaction temperature. The DS_{Tos} initially increases with increasing reaction temperature, reach a maximum value of 1.44 at reaction temperature of 25 °C, then a decrease in DS_{Tos} is observed. This observation may be explained as an increase in reaction temperature contributed to accelerating the reaction rate, and higher temperature caused more side reaction, these two contradictory effects resulted in the observed DS_{Tos} change.

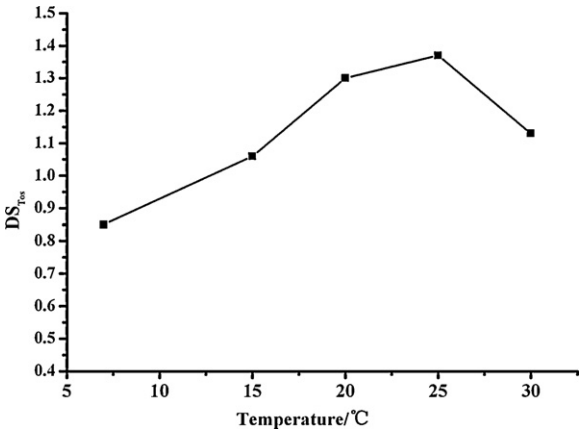

Fig. 6. Effect of reaction temperature on DS_{Tos}. (The mole ratio of TsCl:ASU is 1:2.5, and the reaction time is 10 h.)

3.4.3. Effect of reaction time on the DS_{Tos}

The effect of reaction time on the DS_{Tos} is showed in Fig. 7. It was found that the DS_{Tos} rapidly increased to 1.40 within 10 h, and then levels off with increasing reaction time. By increasing the reaction time to 24 h, the DS_{Tos} is only increased to 1.43. This suggests that the reaction can reach equilibrium within 10 h.

The experimental results came to a conclusion that the DS_{Tos} can be easily controlled by adjusting the mole ratio of TsCl to ASU, reaction temperature and reaction time.

3.5. Effects of reaction conditions on the preparation of EAHPG

In this study, ethanolamine was acted as both aminating reagent and the solvent to dissolve the HPG-Tos. Consequently, abundant of ethanolamine was used in the nucleophilic substitution reaction (S_N) of tosyl groups with ethanolamine, in which the mole ratio of ethanolamine to the tosyl groups in HPG-Tos was chose to be 30:1.

3.5.1. Effect of temperature on the S_N reaction

The S_N reaction of tosyl group with ethanolamine was carried out at 30 °C, 40 °C and 50 °C for 24 h, respectively. As shown in Table 1, the nitrogen content of EAHPG increased with the increase of reaction temperature, indicating the reaction temperature has an important effect on improving the S_N reaction rate of tosyl group with ethanolamine. However, higher temperature may lead to an increase in degradation of EAHPG and substitution of ethanolamine, the temperature of 50 °C is considered as a suitable temperature to proceed the substitution reaction of tosyl group by ethanolamine.

Table 1
Effect of reaction conditions on the S_N reaction.

Sample	Temperature/°C	Time/h	$Wt_{(N)}$[a]/%	$Wt_{(N)}$[b]/%
1	30	24	3.58	3.43
2	40	24	3.89	3.78
3	50	2	2.81	2.68
4	50	5	3.47	3.43
5	50	8	3.85	3.78
6	50	10	3.99	3.93
7	50	24	4.02	3.95

[a] $Wt_{(N)}$ was determined by element analysis.
[b] $Wt_{(N)}$ was determined by acid–base titration.

3.5.2. Effect of reaction time on the S_N reaction

As can be seen from Table 1, increasing reaction time was beneficial for the S_N reaction of tosyl groups with ethanolamine. The nitrogen content of EAHPG increased with increasing reaction time and reached a constant value at 10 h, indicating that the S_N reaction of tosyl groups with ethanolamine was completed.

4. Conclusions

HPG-Tos can be prepared by reacting HPG with tosyl chloride in pyridine, the tosyl group on HPG-Tos can be further displaced by ethanolamine to obtain guar gum derivative containing amino group. The DS of tosyl groups of HPG-Tos could be easily controlled by varying reaction temperature, reaction time and the mole ratio of TsCl to ASU in the reactions. For the substitution reaction of tosyl groups with ethanolamine, reaction time and temperature have an important effect. The experiments results show that the tosyl groups can be effectively substituted by ethanolamine after reacting for 10 h at 50 °C, and EAHPG with high degree of substitution of amino group can be obtained. The DS of amino group in EAHPG as monitored by nitrogen content can be effectively controlled by varying the DS of tosyl group in the HPG-Tos.

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