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Homogeneous synthesis of hydroxypropyl guar gum in an ionic liquid 1-butyl-3-methylimidazolium chloride

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ABSTRACT

With potassium hydroxide (KOH) as catalyst, hydroxypropyl guar gum (HPG) was successfully prepared under homogenous conditions in an ionic liquid 1-butyl-3-methylimidazolium chloride (BmimCl). The value of degree of molar substitution (MS) of HPG, which was determined by means of ^{1}H NMR, was easily controlled by varying the mass ratio of propylene oxide (PO) to guar gum (GG). The distribution of hydroxypropyl moieties among the seven hydroxy groups in HPGs was investigated by NMR and the results indicated that the homogeneous reaction preferentially substituted at the C_3—OH of the mannosyl residues in guar gum which was quite different from the heterogeneous reaction where substitution mostly occurred at C_6—OH. The average number of hydroxypropyl units per OH substitution of HPGs with MS value of 0.20, 0.37 and 0.60 was 1.82, 1.42 and 1.76, respectively.

1. Introduction

Guar gum is a polysaccharide consisting of a backbone of 1,4-linked β-D-mannopyranosyl units with branches of 1,6-linked α-D-galactopyranosyl units (McCleary, Clark, Dea, & Rees, 1985). So it can be chemically modified to improve its physical and chemical properties. Hydroxypropyl guar gum, one of the most important derivatives, is prepared from the native guar gum via an irreversible nucleophilic substitution using propylene oxide (PO) in the presence of an alkaline catalyst (Lapasin, De Lorenzi, Pricl, & Torriano, 1995). The reaction is always carried out in a heterogeneous way using organic solvents which have harmful impact on environment (Venkataiah & Mahadevan, 1982). Therefore, homogeneous modifications of guar gum, in particular in green solvents, have received much attention because the homogeneous reactions proceed efficiently and uniformly in a homogeneous manner.

Ionic liquids (ILs) which are considered as green solvents have attracted the attention of both the academic and the industrial communities in recent years due to their advantages such as excellent dissolution ability, chemical and thermal stability, negligible vapor pressure and ease of recycling (Welton, 1999). Due to their unique properties, ILs seem to be an attractive alternative to conventional volatile organic solvents. Recently, ILs have been found to dissolve carbohydrates such as cellulose (Swatloski, Spear, Holbrey, & Rogers, 2002). A few investigations into the homogeneous modification of polysaccharides in ILs have been reported (Cao et al., 2007, 2009; Liu, Zhang, Li, Yue, & Sun, 2009).

In this study, GG was found to be soluble in an ionic liquid BmimCl. HPGs with different MS values were prepared under homogeneous reaction conditions with KOH as the catalyst in BmimCl. Furthermore, the distribution of hydroxypropyl moieties among the seven hydroxy groups in HPGs was investigated by ^{13}C NMR.

2. Experimental

2.1. Materials

Guar gum used in this study, in which the ratio of moieties of galactose to mannose is 2:3 as determined by ^{1}H NMR spectroscopy, was kindly provided by the Jingkun Oilfield Chemistry Company, Jiangsu, China. 1-Methylimidazole and butyl chloride were available commercially. All other reagents were of analytical grade and used as received.

2.2. Pretreatment of guar gum

The guar gum was extracted by ethanol at 85 °C for 72 h in a Soxhlet extractor and was then dried under vacuum at 40 °C for 48 h.

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2.3. Synthesis of BmimCl

1-Methylimidazole and butyl chloride at a molar ratio 1:1.1 were added to a round-bottomed flask fitted with a reflux condenser and heated at 80 °C for 24 h under stirring (Swatloski et al., 2002). Then the mixture was cooled to room temperature, washed several times with ethyl acetate, concentrated by rotary evaporation and dried under vacuum at 100 °C for 2 h.

2.4. Homogeneous hydroxypropylation of guar gum in BmimCl

In a glass bottle fitted with a magnetic stirrer, the guar gum was added to BmimCl at a concentration of 2% (w/w). Then the reaction vessel was sealed, inserted into a syringe needle and evacuated for 15 min. After that, potassium hydroxide solution was added to the bottle and then the mixture was heated to 80 °C for 2 h resulting in a homogeneous transparent solution. Subsequently, propylene oxide was introduced with a syringe and the reaction was carried out at 80 °C for 8 h.

Once the reaction had finished, the formed HPG was precipitated by addition of a 20-fold amount of 85% (v/v) acetone–H_2O mixture and the resulting mixture was separated by centrifugation. The solid was washed several times and dried under vacuum at 60 °C for 1 h.

2.5. NMR characterization of products

The ^1H NMR and ^{13}C NMR spectra were recorded at 298 K with a Bruker Avance 600 MHz spectrometer. The chemical shifts were given in ppm relative to the internal standard TMS.

Prior to the ^1H NMR measurements, the samples were fully hydrolyzed in the 10% DCl–D_2O (v/v) solution at 100 °C for 15 min. Before the ^{13}C NMR measurements, the samples were capable of complete hydrolysis in the 3% DCl–D_2O (v/v) solution at 100 °C for 4 h.

3. Results and discussion

3.1. Determination of the degree of molar substitution

The degree of molar substitution (MS) represents the extent of the reaction and largely determines the physical and chemical properties of HPG. The MS value of HPG is defined as the number of moles of combined propylene oxide per monosaccharide unit which was determined by means of ^1H NMR spectroscopy. The MS value of HPG could be calculated according to Eq. (1).

$$\mathrm{MS} = \frac{(1/3) \times I_{\mathrm{methyl}}}{I_{\mathrm{anomeric}}} \tag{1}$$

where, I_{methyl} is the integral of hydrogen atoms of methyl group in hydroxypropyl moieties; I_{anomeric} is the integral of all the hydrogen atoms of anomeric carbons in guar gum molecule; the 1/3 is because the methyl group of hydroxypropyl moieties has three hydrogen atoms.

Fig. 1 shows a ^1H NMR spectrum of HPG with MS value of 0.20 in which the signals at from 1.0 ppm to 1.44 ppm were attributed to the hydrogen atoms of methyl group in hydroxypropyl moieties and from 4.5 ppm to 5.5 ppm to the hydrogen atoms of anomeric carbons of both galactosyl and mannosyl residues. The MS value of this sample was obtained by Eq. (1).

$$\mathrm{MS} = \frac{(1/3) \times 1.00}{1.63} = 0.20$$

Table 1
The conditions and results of the homogeneous reaction.

No.	PO/GG (mass ratio)	MS
HPG-1	1.5	0.06
HPG-2	2.5	0.09
HPG-3	3	0.11
HPG-4	12	0.20
HPG-5	24	0.37
HPG-6	36	0.60

The mass ratio of water to GG is 0.6.
The mass ratio of KOH to GG is 0.05.

3.2. Preparation of HPGs with different MS values

As a reaction medium, BmimCl could remain stable at 80 °C with the onset temperature of degradation of 254 °C (Huddleston et al., 2001). On the other hand, GG could be soluble in BmimCl at 80 °C. So the reaction could be carried out at 80 °C. Considering that BmimCl has a high viscosity, water was introduced into BmimCl to reduce the viscosity. KOH was used as catalyst in this reaction.

Table 1 summarizes the conditions and results of the homogeneous reaction. HPGs with different MS values were prepared by varying the mass ratio of PO to GG. It can be seen that the MS value increased as the mass ratio of PO to GG increased from 1.5 to 36. This could be reasonably attributed to increased contact between GG and PO.

3.3. Determination of the degree of substitution

For guar gum, the C_2—OH, C_3—OH, C_4—OH and C_6—OH of galactosyl residues and C_2—OH, C_3—OH and C_6—OH of mannosyl residues could react with PO resulting in hydroxypropyl moieties. The degree of substitution (DS) value, which is defined as the average number of hydroxyl groups substituted per monosaccharide unit, could reflect the distribution of substituent. There is no doubt that the partial DS value among four hydroxyl groups of galactosyl residues and three hydroxyl groups of mannosyl residues has a significant influence on the property of HPG. It could be determined by ^{13}C NMR.

Fig. 2 shows a ^{13}C NMR spectrum of sample HPG-6 with a MS value of 0.60. The signals at from 15 ppm to 22 ppm were attributed to the methyl carbons of hydroxypropyl moieties.

Fig. 3 shows a detailed investigation into the signals between 60 ppm and 96 ppm. The hydrolysis products of HPG were galactosyl and mannosyl residues. Both galactose and mannose contain α-anomer and β-anomer. The signal at 96.1 ppm was attributed to C_1 of β-anomer of galactosyl residues (Gβ1), 93.7 ppm to that of α-anomer of mannosyl residues (Mα1), 93.4 ppm to that of β-anomer of mannosyl residues (Mβ1) and 92.0 ppm to that of α-anomer of galactosyl residues (Gα1). The signals are assigned as shown in Table 2 (Gorin & Mazurek, 1975). It can be found that the signal intensities of Gβ1, Mα1, Mβ1 and Gα1 in HPGs with different MS values almost keep constant, which indicates that the degree of substitution of C_2—OH (DS_2) of GG was low enough to neglect the impact on C_1 of substituted C_2. So the degree of substitution of C_2—OH of galactosyl residues (DS_{G2}) and that of C_2—OH of mannosyl residues (DS_{M2}) could be calculated according to Eqs. (2) and (3).

$$DS_{G2} = 1 - \frac{I_{G\alpha 2} + I_{G\beta 2}}{I_{G\alpha 1} + I_{G\beta 1}} \tag{2}$$

$$DS_{M2} = 1 \frac{I_{M\alpha 2} + I_{M\beta 2}}{I_{M\alpha 1} + I_{M\beta 1}} \tag{3}$$

where, $I_{G\alpha 2} + I_{G\beta 2}$ is the integral of unsubstituted C_2 of the galactosyl residues; $I_{G\alpha 1} + I_{G\beta 1}$ is the integral of all the C_1 of the galactosyl

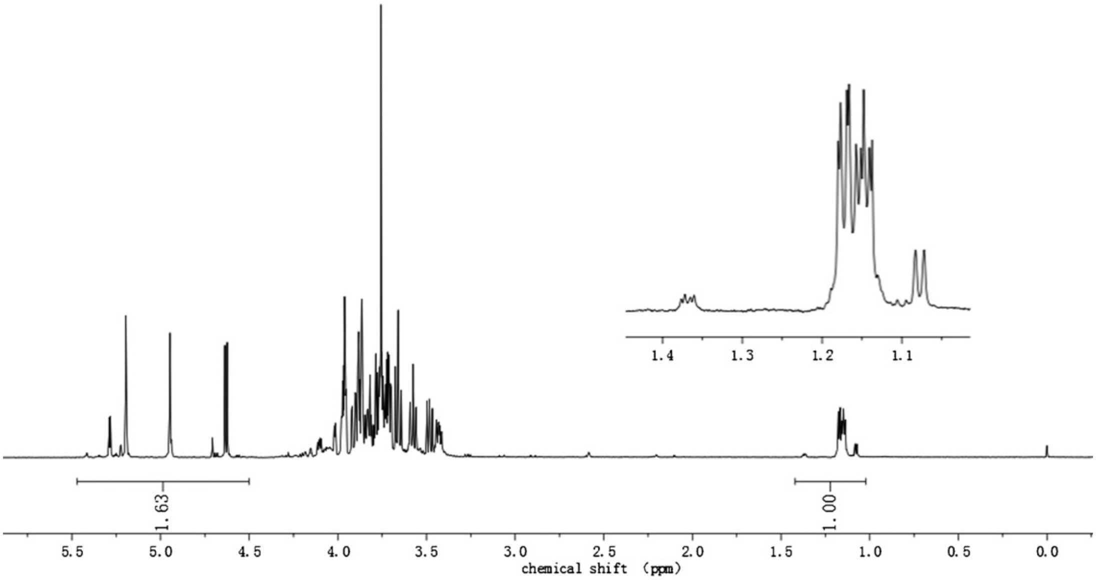

Fig. 1. ^{1}H NMR spectrum of HPG-4 for the determination of MS value.

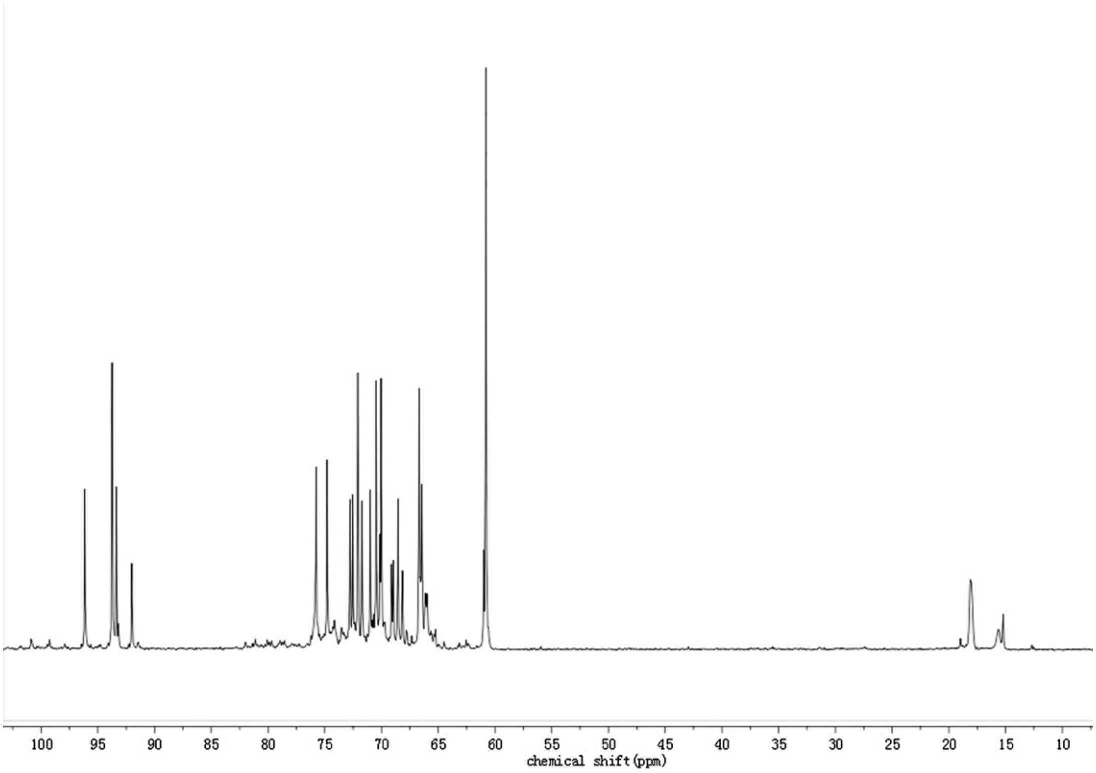

Fig. 2. ^{13}C NMR spectrum of HPG-6.

residues; $I_{M\alpha 2}+I_{M\beta 2}$ is the integral of unsubstituted C_2 of the mannosyl residues; $I_{M\alpha 1}+I_{M\beta 1}$ is the integral of all the C_1 of the mannosyl residues.

DS_2 could be obtained according to definition (Eq. (4)).

$$DS_2 \equiv \frac{n(C_2\text{—OH})}{5x} = \frac{n(C_{G2}\text{—OH}) + n(C_{M2}\text{—OH})}{5x} = \frac{DS_{G2} \times 2x + DS_{M2} \times 3x}{5x} = \frac{DS_{G2} \times 2 + DS_{M2} \times 3}{5} \quad (4)$$

where, $n(C_2\text{—OH})$ is the number of C_2—OH substituted; x is the number of repeating unit of guar gum; $n(C_{G2}\text{—OH})$ is the number of C_2—OH of galactosyl residues substituted; $n(C_{M2}\text{—OH})$ is the number of C_2—OH of mannosyl residues substituted.

DS_3, DS_4, DS_6 could be obtained using the same method as DS_2. DS was calculated as $DS_2+DS_3+DS_4+DS_6$. All the results are presented in Table 3. It can be seen that all the partial DS values increase with an increase of MS.

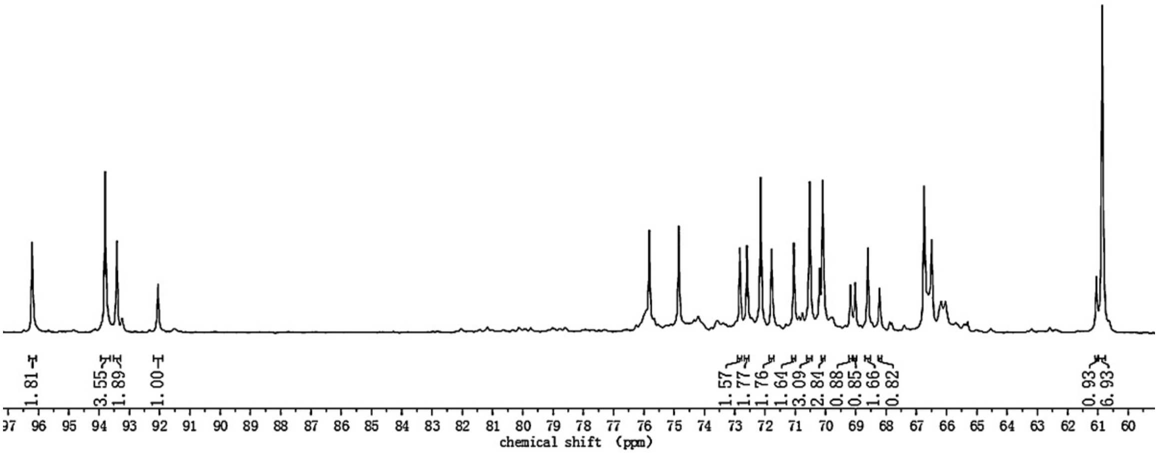

Fig. 3. ^{13}C NMR spectrum of HPG in detail range from 60 ppm to 96 ppm.

Table 2
Assignments of ^{13}C NMR spectrum of HPGs.

Chemical shift (ppm)	Assignments	Intensity[a]	Intensity[b]	Intensity[c]
96.1	Gβ1	1.85	1.83	1.81
93.7	Mα1	3.56	3.52	3.55
93.4	Mβ1	1.84	1.88	1.89
92.0	Gα1	1.00	1.00	1.00
72.7	Mβ3	1.72	1.58	1.57
72.5	Gβ3	1.83	1.81	1.77
71.7	Gβ2	1.84	1.81	1.76
71.0	Mβ2	1.81	1.69	1.64
70.4	Mα2	3.52	3.27	3.09
70.0	Mα3	3.26	2.89	2.84
69.1	Gα4	0.94	0.92	0.88
68.9	Gα3	0.97	0.89	0.85
68.5	Gβ4	1.80	1.74	1.66
68.1	Gα2	1.00	0.90	0.82
60.9	Gα6	0.94	0.92	0.93
60.8	Gβ6 + Mα6 + Mβ6	7.00	6.94	6.93

G: galactose; M: mannose.
[a] HPG-4.
[b] HPG-5.
[c] HPG-6.

Apparently, DS_{M3} is much larger than the other partial DS values. This indicates that the C_3—OH of the mannosyl residues in GG has the strongest reaction activity for the homogeneous reaction.

It should be noticed that the distribution of hydroxypropyl moieties is quite different from HPG samples synthesized industrially through heterogeneous process.

Bin Ding (Ding, Cheng, Wang, Luo, & Jiang, 2008) found that DS_6 value of HPGs with MS value of 0.34 and 0.62 is 0.24 and 0.40 using the TEMPO-mediated method. His research results showed that the substitution mostly occurred at C_6—OH of guar gum. This is quite different from the homogeneous reaction because the DS_6 value of HPGs with MS value of 0.37 and 0.60 is 0.05 and 0.05 (Table 3). To speak more precisely, the PO is inclined to react with the C_3—OH of the mannosyl residues in GG.

Furthermore, by calculating the ratio of the MS value and the DS value, the average number of hydroxypropyl units per OH substitution of HPGs with MS value of 0.20, 0.37 and 0.60 is 1.82, 1.42 and 1.76, respectively.

Table 3
Distribution of hydroxypropyl moieties among seven hydroxyl groups in HPGs.

Sample (MS)	HPG-4 (0.20)	HPG-5 (0.37)	HPG-6 (0.60)
DS_{G2}	0.00	0.04	0.08
DS_{G3}	0.02	0.05	0.07
DS_{G4}	0.04	0.06	0.10
DS_{M2}	0.01	0.08	0.13
DS_{M3}	0.08	0.17	0.19
DS_2	0.01	0.07	0.11
DS_3	0.05	0.12	0.14
DS_4	0.02	0.02	0.04
DS_6	0.03	0.05	0.05
DS	0.11	0.26	0.34

4. Conclusions

HPG was successfully prepared under homogeneous conditions using an ionic liquid BmimCl as a reaction medium. The MS value of HPG which was determined by means of ^{1}H NMR increased with an increase of the mass ratio of PO to GG. The homogeneous reaction showed a preference at the C_3—OH of the mannosyl residues in guar gum which was quite different from that the substitution mostly occurred at C_6—OH of guar gum in the heterogeneous reaction. The average number of hydroxypropyl units per OH substitution of HPGs with MS value of 0.20, 0.37 and 0.60 is 1.82, 1.42 and 1.76, respectively.

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