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Selective oxidation and determination of the substitution pattern of hydroxypropyl guar gum

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ABSTRACT

The substituent distribution in hydroxypropyl guar gums was characterized by chemical methods in this study. A new method based on periodate oxidation combined with probability analysis was proposed to determine the degree of substitution at secondary hydroxyl groups. The periodate oxidation was investigated at pH = 4.3 and at the temperature of 25 °C. The oxidized products were characterized by IR and NMR. It was shown that carbonyl groups in oxidized products were in the form of hemiacetal. The degree of substitution at primary hydroxyl groups was determined by the reaction of 2, 2, 6, 6-Tetramethyl-1-piperidinyloxy radical (TEMPO)-mediated selective oxidation. Therefore, the total degree of substitution and the average length of hydroxypropyl substituents were calculated. Results showed that the values of the total degree of substitution (DS) were practically the same as the values of molar substitution (MS) in the range of 0.2–1.5. The average chain length of hydroxypropyl substituents was almost 1.0.

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1. Introduction

Hydroxypropyl guar gum (HPG) is widely used in many industrial sectors such as oil recovery, food systems, paints, mineral industry and personal care, etc. (Seaman, 1980). Compared with native guar gum, HPG has better solubility and thermal stability in solution. HPG is prepared from native guar gum via an irreversible nucleophilic substitution, using propylene oxide in the presence of an alkaline catalyst (Lapasin, Lorenzi, Pricl, & Torriano, 1995). The chemical and functional properties of HPG are mainly dependent on the pattern of substitution, the distribution of the substituent and the average length of the hydroxypropyl substituents (DPn) (Ho, Kohler, & Ward, 1972). The MS of HPG can be determined by means of ^{1}H-NMR or ^{13}C-NMR spectroscopy. However, it is difficult to determine the distribution pattern of substituent of HPG because of the heterogeneity of their structures and the low resolution and difficulties of NMR spectra resonances assignment. Several analytical methods have been developed over the years for the determination of the distribution of substituents of the hydroxypropyl group. Reuben established a statistical kinetic model to describe the substituents of HPG (Reuben, 1985). Gas–liquid chromatography with mass (GLC–MS) spectrometry was also used to determine the substituent distribution in hydroxypropylated potato amylopectin (Richardson, Nilsson, Bergquist, Gorton, & Mischnick, 2000). This procedure was employed as the standard method of testing.

Periodate oxidation has been widely used as a routine method for structural analysis of carbohydrates (Bruneel & Schacht, 1993; Uraz & Güner, 1997). It is well known that the reaction leads to selective cleavage of the carbon–carbon bond of adjacent diols and converts them to dialdehyde groups without significant side reactions. In addition to the adjacent diols, other 1, 2-dioxygenated groups and 1, 2-aminoalcohols are also oxidatively cleaved by the periodate (Nicolet & Shinn, 1939). The adjacent diols which are substituted by etherifying agents including methyl, carboxymethyl and hydroxypropyl are prevented from cleavage by periodate ions (Edward Glass et al.,1980; Vold & Christensen, 2005). According to this method, the content of adjacent hydroxyl groups in the carbohydrate derivatives, such as carboxymethyl cellulose (Dyer & Arnold, 1952) and methyl starch (Moe, Miller, & Buckley, 1951) can be determined by consumption of periodate ions, and then the degree of substitution at the secondary hydroxyl groups (DS_S) can be evaluated.

In the present work, periodate oxidations of GG and HPG were systematically studied as well as the kinetics and stoichiometry of the reaction. Oxidized GG and HPG were characterized by NMR and IR. The DS_S values of a series of hydroxypropyl guar gums with different molar degrees of substitution were calculated by the results of periodate oxidation and probability theory. The degree of substitution at primary hydroxyl groups (DS_P) was determined by TEMPO-mediated oxidation previously established (Ding et al.,

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2008). The total DS and DPn of HPG were analyzed and discussed. In order to view the applicability of this analysis method, the substitution degree at the secondary hydroxyl groups (DS_S) and the content of adjacent hydroxyl groups of methyl cellulose (MC) were determined by this method and compared with results obtained by NMR.

2. Experimental

2.1. Materials

Guar gum (GG, Mn = 2.5×10^6 g/mol) and hydroxypropyl guar gums (HPG, 2.35×10^6–1.79×10^6 g/mol) with different MS (0.25–1.54) were kindly provided by the Jingkun Oilfield Chemistry Company, Jiangsu in China. All guar gum and hydroxypropyl guar gums were purified by dissolving in water and precipitation with ethanol. The polysaccharides were treated with 1.0 mol/L HCl at the temperature of 60 °C for 1 h with continuous stirring in order to degrade the samples into lower molecular weight polymer, and the Mn values of the partially hydrolyzed samples were in the range of 2.0×10^5–3.0×10^5 g/mol. The average molecular weight of hemi-degraded samples was determined by gel permeation chromatography (GPC) with a Shimadzu instrument (column, Tosoh TSK Gel G4000pwxl; and G3000pwxl; eluent, 0.02% NaN_3 aqueous solution; 40 °C; flow rate, 0.5 ml/min; Brookhaven Technology BI-MwA multi-angle light scattering detector and BI-DNDC RI detector). The ratio of G to M and the MS of HPG were determined by ^1H NMR spectroscopy. Sodium periodate, sodium thiosulfate, acetone and dimethyl sulfoxide (DMSO) are all analytical grade reagents.

2.2. periodate oxidation of GG and HPG

The oxidation reaction of GG or HPGs was carried out in buffer solution at 25 °C. 0.5 g starting material was dissolved in 100 ml CH_3COO^-/CH_3COOH (pH = 4.2, 0.1 mol/L) buffer solution under magnetic stirring over night. Then the solution of sodium periodate (10 ml, 100 g/L) was added under stirring, reaching a final volume of 250 ml with distilled water. The analysis of the periodate solution were carried out at various time intervals by titration with sodium thiosulfate in phosphate buffer solution (pH = 7.0, 0.5 M) with starch as an indicator as the method reported by Ishak (Ishak & Painter, 1973). After 72 h, the reaction was terminated by the addition of ethylene glycol (5.0 ml) under stirring for 0.5 h. Then the water was removed by evaporation under vacuum at 60 °C. The oxidized GG (HPG) was again dissolved in 50 ml DMSO and precipitated by the addition of 1 L acetone. Finally, the precipitate was washed with acetone several times until no salt remained, and dried at room temperature under vacuum. Each reaction was performed three times under the same condition and the average value was used for final analysis.

2.3. TEMPO-mediated oxidation of GG and HPG

The procedure of TEMPO-mediated oxidation was followed by the method published earlier (Ding et al., 2008).

2.4. FTIR spectra

The IR spectra were obtained from samples in KBr pellets using a Thermo Nicolet 670FT-IR spectrophotometer.

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

^{13}C and ^1H NMR spectra were recorded on a AVANCE III 600 MHz Digital NMR Spectrometer (Probehead:Broadhand Probehead BB-H-D 5 mm) using D_2O (99.7%) as the solvent.

3. Results and discussion

3.1. FTIR spectrum and NMR spectrum

Fig. 1a shows the mechanism of periodate oxidation of GG. Hydroxyl groups on carbons 2, 3, 4 of the repeating unit were oxidized by sodium periodate which leads to the formation of two aldehyde groups in each oxidized monomeric unit by cleavage of carbon–carbon bond. In the structure of HPG, the hydroxyl groups substituted by hydroxypropyl residue will not react with periodate ions (Fig. 1b).

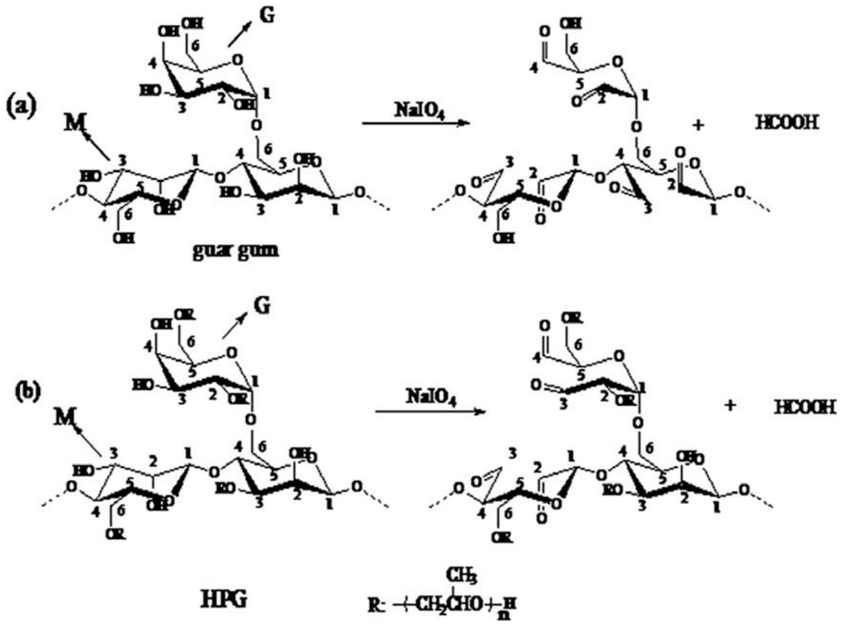

Fig. 1. The mechanisms of periodate oxidation of GG (a) and HPG (b).

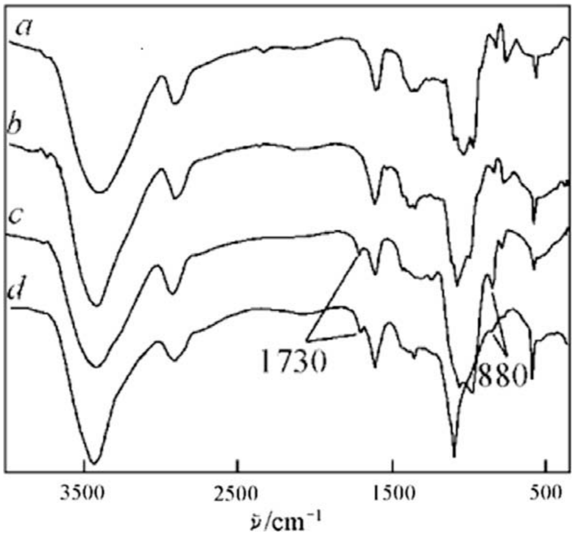

Fig. 2. IR spectrum of GG (a), HPG (b), oxidized GG (c) and oxidized HPG with MS = 0.25(d).

The changes of the GG and HPG after periodate oxidation were examined by FTIR and NMR. Fig. 2 shows the FTIR spectrum of native GG (a), HPG (b),oxidized GG(c) and HPG (MS = 0.25, d). The characteristic bands of oxidized products appeared in the 1730 and 880 cm^{-1} regions. Because most carbonyl groups in the molecular structure are in the form of hemiacetal (Kim, Kuga, Wada, Okano, & Kondo, 2000; Zhang et al., 2007), there is only a small absorbance of carbonyl groups appears at about 1730 cm^{-1}. The band around 880 cm^{-1} is generally assigned to the formation of hemiacetal and hydrated bonds between the aldehyde groups and hydroxyl groups (Kim et al., 2000), which indicateds that the adjacent hydroxyl groups in GG and HPG have been oxidized to dialdehyde by periodate oxidation.

Fig. 3 shows ^{1}H-NMR spectrum of the oxidized GG and HPG. There is a small resonance at 9.30 ppm in the spectra of oxidized samples, indicating that carbonyl groups are present after the oxidation but not all remain free. The appearance of new signals region from 4.5 to 5.0 should be attributed to hemiacetalic protons formed from aldehyde and neighbors hydroxyl groups besides solvent peak (Gomez, Rinaudo, & Villar, 2007). The peak area of signal at 1.15 ppm due to the methyl groups of hydroxylpropyl guar gum shows little change after oxidation. It can be concluded that the substitution residues are not affected during the periodate oxidation process.

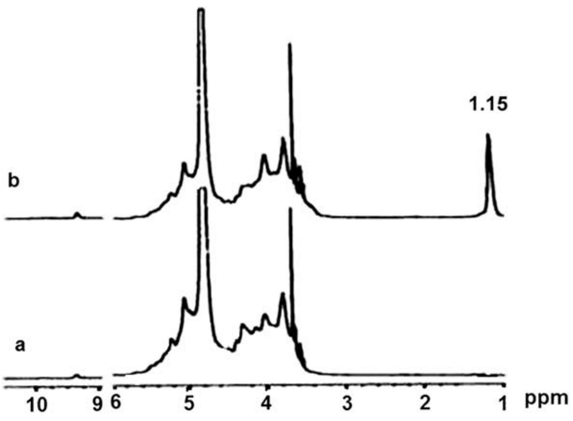

Fig. 3. ^{1}H-NMR spectrum of oxidized GG (a) and HPG (b) with MS = 0.25.

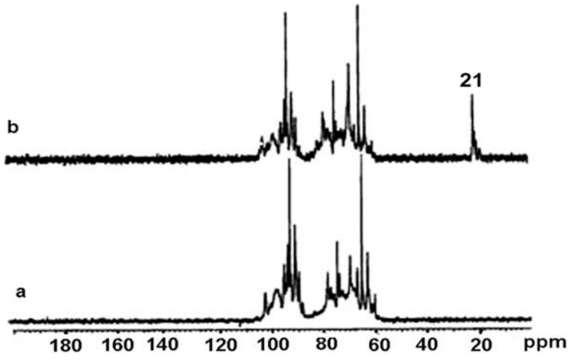

Fig. 4. ^{13}C-NMR spectrum of oxidized GG (a) and HPG (b) with MS = 0.25.

Similar conclusion can be found in the ^{13}C-NMR spectrum (Fig. 4). Compared with native HPG, there is no obvious change in the oxidized HPG (Fig. 4b) at 21 ppm which corresponds to methyl groups of hydroxypropyl. The carbonyl signal expected at 190–195 ppm can not be found, which indicates that the aldehyde groups of oxidized products are hydrated or forming hemiacetals with remaining hydroxyl groups. On the other hand, the appearance of new signals in the region of 90–95 ppm should be attributed to hemiacetalic carbons corresponding to aldehyde groups generated (Gomez et al., 2007). These results show that the adjacent hydroxyl groups in the GG and HPG have been oxidized to carbonyl groups, and the carbonyl groups are in the form of hemiacetals.

3.2. The procedure of periodate oxidation

Fig. 5 shows the kinetic courses of periodate oxidation of GG and HPGs with different MS (MS = 0.25, 0.51, 0.78, 1.05 and 1.54) by an excess of periodate at 25 °C. The oxidation reaction is relatively quick at the beginning, then the reaction rate decreases asymptotically. Values of periodate consumption per mole monosaccharide unit (Pt, mol%) show no obvious increase after 72 h. The same kinetic behaviors were observed for all the oxidation experiments in this work. The final consumption of periodate dependent on the MS, for reason that HPG with low MS consume more periodate than highly substituted products. These observations indicate that polysaccharide substituted by propylene oxide

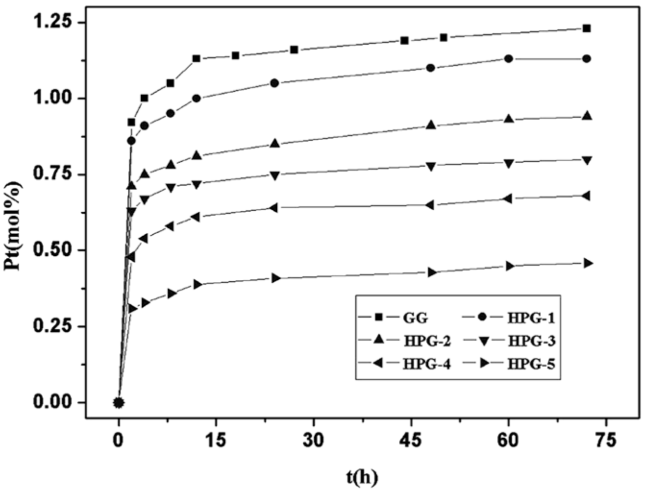

Fig. 5. The kinetic courses of periodate oxidation of GG and HPGs with MS = 0.25, 0.51, 0.78, 1.05, 1.54.

will reduce the consumption of periodate as long as the substitution occurs at adjacent hydroxyl groups.

GG consists of galactopyranose (G) and mannopyranose (M) and the ratio of G to M is 1:1.8 determined by ^{1}H-NMR. The maximum value of Pt is 1.357 calculated in theory. The periodate oxidation must proceed to 100% to ensure the accuracy of the quantitative determination of DS_S. Several oxidation experiments were conducted for the unsubstituted guar gum. Experiment values of Pt are generally less than the theoretical maximum value, about 1.23, and the oxidation degrees are about 90% after reacting 72 h. This behavior can be related to hemiacetal formatio, for high concentration of aldehyde groups in oxidized uronic solution, and these groups can react with hydroxyl groups in the vicinity (Frollini, Reed, Milas, & Rinaudo, 1995; Painter & Larsen, 1970; Smidsrød & Painter, 1973). The formation of hemiacetals protects some hydroxyl groups from further oxidation and delays the reaction process (Ishak & Painter, 1973). In this case, the oxidation procedure can't reach the end point, after 72 h the reactions have reached the equilibrium, so the reactions are stopped at 72 h. Each experiment was performed three times and was reproducible with a standard deviation which did not exceed 3%.

3.3. Determination of DS_S for HPG

As the experiment values of Pt is less than the theoretical values for unsubstituted guar gum. To correct this systematic deviation of Pt, the values of Pt were treated as follows (Eq. (1)), with the assumption that all the products have the same possibility of side reaction.

$$Pt_{(HPG-T)} = \frac{Pt_{(GG-T)}}{Pt_{(GG-E)}} \times Pt_{(HPG-E)} \tag{1}$$

$Pt_{(HPG-T)}$ is the theoretical values for Pt of HPG, which is equal to molar content of adjacent hydroxyl groups; $Pt_{(GG-E)}$ and $Pt_{(HPG-E)}$ are the molar consumption of periodate per mole of monosaccharide after 72 h reaction; $Pt_{(GG-T)}$ is the theoretical value for Pt of GG, which is 1.357 (mol periodate/mol monosaccharide unit).

The probability analysis was also cited to evaluate the DS_S. The calculation procedure was according to the statistical kinetic model of Reuben and its reaction relative constants (Reuben, 1984; Reuben, 1985). Here a brief description of the evaluation steps was introduced. For any given position j of monosaccharide unit I one can write the reaction:

$$\underset{P_{Ij}}{-\mathrm{C}_{Ij}}-\mathrm{OH} + \mathrm{RX} \xrightarrow{k_{Ij}} -\mathrm{C}_{IJ}-\mathrm{OR} + \mathrm{HX}$$

Where k_{Ij} is the reaction relative rate constant of the hydroxyl at position j of monosaccharide I; P_{Ij} is the probability of unsubstituted hydroxyls. The probability of substitution at position j of monosaccharide I can be described as:

$$X_{Ij} = W_I - P_{Ij} = W_I(1 - e^{-Bklj}) \tag{2}$$

Where *WI* is the mole fraction of the monosaccharide unit of type I; *B* is time factor. The total (average) degree of substitution is

$$DS = \sum_I \sum_j X_{Ij} \tag{3}$$

The degree of substitution at secondary hydroxyl groups is

$$DS_S = \sum_I \sum_j X_{Ij} \quad j = 2, 3, 4 \tag{4}$$

Similarly, the probability of unsubstituted adjacent hydroxyl groups at position j and m is:

$$V_{Ijm} = W_I e^{-B(k_{Ij} - k_{Im})} \tag{5}$$

Here j and m must be adjacent, like C_2–C_3 in M, C_2–C_3 and C_3–C_4 in G.

Then the total content of adjacent hydroxyl groups is:

$$V = \sum_I \sum_{j,m} V_{Imj} = \sum_I \sum_{j,m} W_I e^{-B(k_{Ij} - k_{Im})} \tag{6}$$

The adjacent hydroxyl groups consume the same content of periodate via oxidation reaction, viz.

$$V = Pt_{(HPG-T)} \tag{7}$$

Thus, combined with the formula Eq. (1), Eq. (4), Eq. (6) and Eq. (7), the degree at secondary hydroxyl groups DS_S can be determined by the values of $Pt_{(HPG-E)}$ combining with the relative rate constants *k*. To simplify the calculation, it was first assumed that the k value of hydroxyl group at any position was equal to each other.

$$k_{G2} = k_{G3} = k_{G4} = k_{M2} = k_{M3} \tag{8}$$

And the DS_S can be calculated as:

$$DS_S = \sum_I \sum_j X_{Ij}(j = 2, 3, 4) = 2.357 \times \left(1 - \sqrt{\frac{Pt_{(HPG-T)}}{1.357}}\right) \tag{9}$$

To compare the accuracy of the assumption of equal reactivity, the *k* values extracted by Jacques Reuben (1985) were also introduced:

$$k_{M2} : k_{M3} : k_{M2'} : k_{M3'} : k_{G2} : k_{G3} : k_{G4} = 4.21 : 2.47 : 4.54 : 2.22 : 2.17 : 2.55 : 1 \tag{10}$$

Considering the complicacy of calculation process, the DS_S was calculated by computer.

Table 1 shows the results of DS_S determined by periodate oxidation for a series of hydroxypropyl guar gum samples with different MS. Results show that the DS_S values calculated by the two different assumptions (Eqs. (9) and (10)) are the almost same. This indicates that the total degree of substitution at secondary hydroxyl position is not affected by the difference of rate constant *k* for hydroxyl groups at MS less than 1.5. Thus the assumption of equal probability was used in this work.

To analysis the substituent distribution of HPG, the degree of substitution at primary hydroxyl position DS_P was also determined by the method of TEMPO-mediated oxidation. The total degree of substitution DS is the sum of DS_S and DS_P, and the average length of substituent chains can be calculated as:

$$DPn = \frac{MS}{DS} = \frac{MS}{DS_S + DS_P} \tag{11}$$

A summary of data of substitution pattern of HPGs is given in Table 2. Results show that DS_S value is less than DS_P value at low MS. However, DS_S value increases rapidly as MS increase (Fig. 6.). The values of DS were practically the same as MS for all samples, and the average length of substituent chains DPn values are almost

Table 1

DS_S of HPGs with different MS calculated by two different methods.

Sample	MS	$Pt_{(HPG-E)}$ (mol%)	$Pt_{(HPG-T)}$ (mol%)	DS_S[a]	DS_S[b]
GG	0	1.23	1.357	0	0
HPG-1	0.25	1.13	1.25	0.10	0.1
HPG-2	0.51	0.94	1.04	0.30	0.3
HPG-3	0.78	0.8	0.88	0.46	0.46
HPG-4	1.05	0.68	0.75	0.60	0.6
HPG-5	1.54	0.46	0.51	0.92	0.91

[a] Was experimental values respectively calculated according to Eq. (9).

[b] Was experimental values respectively calculated according to Eq. (10).

Table 2
Substitution distribution and DPn of HPGs with MS 0.25, 0.51, 0.78, 1.05, 1.54.

Sample	MS	DS$_S$[a]	DS$_p$[b]	DS	DPn
HPG-1	0.25	0.1	0.14	0.24	1.04
HPG-2	0.51	0.3	0.19	0.49	1.04
HPG-3	0.78	0.46	0.29	0.75	1.04
HPG-4	1.05	0.6	0.36	0.96	1.09
HPG-5	1.54	0.92	0.42	1.34	1.15

[a] Was determined by periodate oxidation.
[b] Was determined by TEMPO-mediated oxidation.

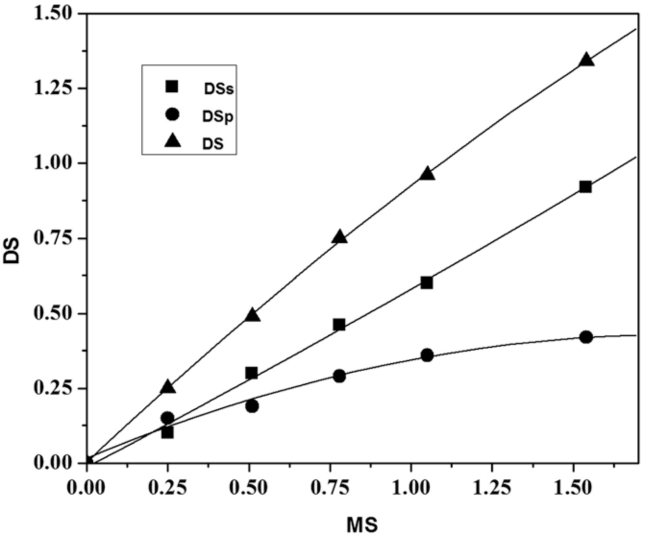

Fig. 6. DS$_S$, DS$_P$ and total DS against MS for HPGs.

1.0, showing that there is almost no chain-extending reaction with propylene oxide at low and medium MS. Longer propylene oxide chain may only appear at sufficiently high MS.

In order to demonstrate the applicability of the method of periodate oxidation, the substitution degree at the secondary hydroxyl groups (DS$_S$) and the content of adjacent hydroxyl groups of methyl cellulose (MC) from this method and instrument analysis were compared. The structure of MC was simpler than that of HPG. The DS of MC on different carbon atoms (C2, C3 and C6) can be ascertained by ^{13}C-NMR spectroscopy (DS$_2$, DS$_3$, DS$_6$). HPLC can be used to determine various substituted carbohydrate units, such as units with no hydroxyl groups substituted, units with one hydroxyl group substituted, units with two hydroxyl group substituted, and units with hydroxyl groups fully substituted. Combining the results from ^{13}C-NMR spectroscopy and HPLC, the substitution degree at the secondary hydroxyl groups (DS$_S$) and the content of adjacent hydroxyl groups can be calculated. Results show that the content of adjacent hydroxyl groups measured by instrument is 0.19, very close to that of Pt values (0.20) determined by periodate oxidation, which indicates that almost all of the adjacent hydroxyl groups have been oxidized and periodate oxidation can accurately determine the content of adjacent hydroxyl groups of MC. The results of ^{13}C-NMR spectroscopy show that DS$_2$ is 0.8, DS$_3$ is 0.4, DS$_6$ is 0.5, so DS$_S$ is 1.2, according to this and combined with Pt values, DS$_S$ of MC is 1.1, the result is in good agreement with that of ^{13}C-NMR spectroscopy.

4. Conclusion

In conclusion, the present techniques using periodate and TEMPO-mediated oxidation have proved to be a convenient and reliable chemical method to determine the substituent distribution of hydroxypropyl guar gum. The results are in good agreement with the values found in the literature by other methods. It is expected that the present technique is applicable for the analysis of substitution pattern of other polysaccharides derivatives.

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References

Bruneel, D., & Schacht, E. (1993). Chemical modification of pullulan: 1. Periodate oxidation. *Polymer, 34*, 2628–2632.

Ding, B., Ye, Y. Q., Cheng, J. C., Wang, K., Luo, J. H., & Jiang, B. (2008). TEMPO-mediated selective oxidation of substituted polysaccharides—an efficient approach for the determination of the degree of substitution at C-6. *Carbohydrate Research, 343*, 3112–3116.

Dyer, E., & Arnold, H. E. (1952). Distribution of hydroxyl groups in carboxymethyl cellulose. *Journal of the American Chemical Society, 74*, 2677–2679.

Edward Glass, J., Buettner, A. M., Lowther, R. G., Stanley Young, C., & Cosby, L. A. (1980). Heterogeneous ethoxylation of cellulose: influence of alkali and available-water concentrations on substituent distributions. *Carbohydrate Research, 84*(2), 245–263.

Frollini, E., Reed, W. F., Milas, M., & Rinaudo, M. (1995). Polyelectrolytes from polysaccharides: selective oxidation of guar gum -a revisited reaction. *Carbohydrate Polymers, 27*, 129–135.

Gomez, C. G., Rinaudo, M., & Villar, M. A. (2007). Oxidation of sodium alginate and characterization of the oxidized derivatives. *Carbohydrate Polymers, 67*, 296–304.

Ho, F. F. L., Kohler, R. R., & Ward, G. A. (1972). Determination of molar substitution and degree of substitution of hydroxypropyl cellulose by nuclear magnetic resonance spectrometry. *Analytical Chemistry, 44*(1), 178–181.

Ishak, M. F., & Painter, T. (1973). The anomalous periodate oxidation limit of guaran. *Acta Chemica Scandinavica, 27*, 1268–1276.

Kim, U. J., Kuga, S., Wada, M., Okano, T., & Kondo, T. (2000). Periodate oxidation of crystalline cellulose. *Biomacromolecules, 1*, 488–492.

Lapasin, R., Lorenzi, L. D., Pricl, S., & Torriano, G. (1995). Flow properties of hydroxypropyl guar gum and its long-chain hydrophobic derivatives. *Carbohydrate Polymers, 28*, 195–202.

Moe, O. A., Miller, S. E., & Buckley, M. I. (1951). Periodate oxidation of the formyl esters of starch. *Journal of the American Chemical Society, 73*, 4185–4186.

Nicolet, B. H., & Shinn, L. A. (1939). The action of periodic acid on α-amino alcohols. *Journal of the American Chemical Society, 61*, 1615.

Painter, T., & Larsen, B. (1970). Formation of hemiacetals between neighboring hexuronic acid residues during the periodate oxidation of alginate. *Acta Chemica Scandinavica, 24*, 813–833.

Reuben, J. (1984). Description and analysis of (hydroxyethyl)cellulose. *Macromolecules, 17*, 156–161.

Reuben, J. (1985). Description of heteropolysaccharide ethers: hydroxypropyl guar and carboxymethyl guar. *Macromolecules, 18*, 2035–2037.

Richardson, S., Nilsson, G. S., Bergquist, K. E., Gorton, L., & Mischnick, P. (2000). Characterisation of the substituent distribution in hydroxypropylated potato amylopectin starch. *Carbohydrate Research, 328*, 365–373.

Seaman, J. K. (1980). Handbook of water-soluble gums and resins. In R. L. Davidson (Ed.). New York: McGraw-Hill.

Smidsrød, O., & Painter, T. (1973). Effect of periodate oxidation upon the stiffness of the alginate molecule in solution. *Carbohydrate Research, 26*, 125–132.

Uraz, I., & Güner, A. (1997). Comparison of molecular association of dextran and periodate-oxidized dextran in aqueous solutions. *Carbohydrate Polymers, 34*, 127–130.

Vold, I. M. N., & Christensen, B. E. (2005). Periodate oxidation of chitosans with different chemical compositions. *Carbohydrate Research, 340*, 679–684.

Zhang, S. D., Zhang, Y. R., Zhu, J., Wang, X. L., Yang, K. K., & Wang, Y. Z. (2007). Modified corn starches with improved comprehensive properties for preparing thermoplastics. *Starch, 59*, 258–268.