Available online at www.sciencedirect.com
SCIENCE DIRECT
Polymer 46 (2005) 12247–12255
polymer
www.elsevier.com/locate/polymer

# Guar gum methyl ethers. Part I. Synthesis and macromolecular characterization

Daniela Risica, Mariella Dentini, Vittorio Crescenzi *

*Department of Chemistry, University of Rome 'La Sapienza', P.le Aldo Moro 5, 00185 Rome, Italy*

Received 7 February 2005; received in revised form 1 August 2005; accepted 17 October 2005
Available online 4 November 2005

**Abstract**

Guar gum (GG) has been partially methyl-etherified under heterogeneous reaction conditions. The resulting products, (methyl ether guar: MG) with different degrees of substitution, have been characterized by means of viscosity, $^1$H NMR, and FTIR measurements. The introduction of methoxyl groups along the polysaccharidic chains reduces the hydrogen bonding sites on the guar backbone reducing primarely the extent of hydrogen bonding between guar macromolecules, hence their aggregation tendency. A comparative analysis of Mark–Houwink–Sakurada parameters and of the characteristic ratio ($C_\infty$) of GG and MG samples in aqueous solution has been carried out using the Burchard–Stockmayer–Fixman method for flexible and semiflexible chains. The MG chains exhibit more flexibility than those of native guar gum which is traceable to a disruption of intrachain hydrogen bonds.


*Keywords:* Guar gum; Methyl ether guar; Solution properties

## 1. Introduction

Guar gum (GG) is a water-soluble polysaccharide extracted from the seeds of the leguminous shrub Cyamopsis Tetragonaloba, where it acts as a food and water reservoir. It belongs to the galactomannan family and its structure, shown in Fig. 1, consists of a (1–4)-linked β-D-mannopyranose backbone with random branchpoints of α-D-galactose units (i.e. (1–6)-linked α-D-galactopyranose residues).

Guar gum possesses a high level of galactose substitution along the mannan backbone (approximately 40%). On the average, there are between 1.5 and 2 mannose residues for every galactose residue, with few, if any, non-substituted regions [1].

GG is widely used in many industrial sectors such as oil recovery [2,3], food [4,5] and personal care [6], owing to its ability to produce highly viscous, pseudoplastic aqueous solutions even at low concentrations. This is due to the high molecular weight typical for this polysaccharide (up to 2 MDa) and to the presence of extensive chains hyperentanglements promoted by hydrogen bonding [7,8]. However, native GG samples upon dissolution in water may give rise to as much as 10–14% insoluble residues depending on the gum purity [9]. Such residues, which in all likelyhood are composed of heavily intertwined polysaccharide chains, proteins and ashes, together with the tendency of GG to form aggregates in solution are undesirable characteristics for some commercial applications. The synthesis and purification of GG derivatives, such as the well known hydroxyalkyl-G and carboxymethyl-G, may obviate said problems and, quite naturally, allow to obtain new products/materials with application oriented bulk and solution properties.

In our laboratory the partial methyl etherification process [10–16] has been optimized having in mind its future scale-up for the industrial production of a non ionic derivative of GG, of likely marketing interest. This derivate has not been studied until today either from a scientific standpoint nor in terms of its potential industrial applications.

The reaction has been carried out in heterogeneous phase to obtain methyl guar (MG) samples with different degrees of substitution (DS). Dilute aqueous solutions of the latter (Scheme 1) and of GG samples have been characterized in a comparative fashion. Using appropriate models, the Mark–Houwink–Sakurada parameters and the characteristic ratio, $C_\infty$, of GG and MG derivatives have been evaluated. The dependence of intrinsic viscosity on temperature has been

* Corresponding author. Tel.: +39 649913630; fax: +39 64457112.
*E-mail address:* vittorio.crescenzi@uniroma1.it (V. Crescenzi).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.10.083

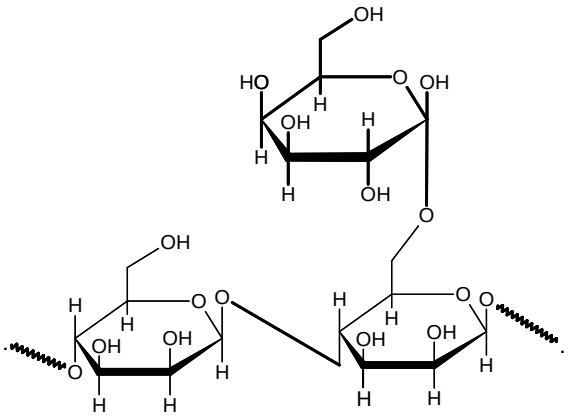


Fig. 1. Structure of guar gum (GG): guar gum has a linear backbone of β-1,4-linked mannose units with α-1,6-linked galactose units attached as side chains.

determined for both GG and MG samples. Solution studies were particularly aimed at shedding light on the effect of primary structure on polysaccharide chain flexibility. The results are reported herein.

## 2. Experimental section

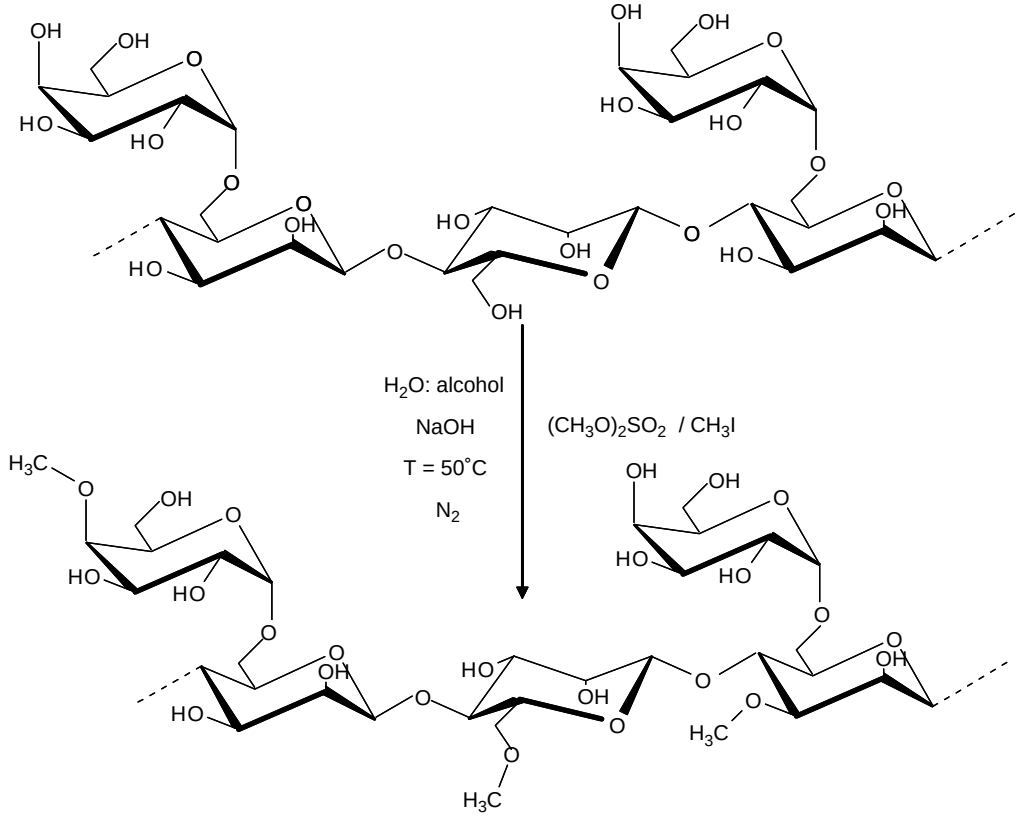
### 2.1. Materials

Guar gum was supplied by Lamberti s.p.a. (Plant and Technological Centre of Albizzate, Italy). Dimethylsulfate (DMS) and methyliodide (MI) were obtained from Sigma-Aldrich and were used as received. All other chemicals were commercially available products used without further purification.

### 2.2. Methylation

The etherification procedure adopted was as follows. The guar gum flour (5 g) was slowly dispersed to form a 50% (w/v) solution in a hydro-alcoholic mixture of isopropyl or ter-butyl alcohol (≈30 mL) in a clean round bottom flask (100 mL) maintained at 25 °C, with constant stirring (600±10 rpm, overhead mechanical stirrer). The resulting heterogeneous mixture was heated to 50 °C and purged with nitrogen for 1 h. A calculated amount of a 50% (w/v) aqueous solution of sodium hydroxide was added to the slurry, and the mixture was stirred for 10 min. The temperature of the reaction was decreased to 35–40 °C and the required amount of alkylating agent (DMS or MI) was then added dropwise under constant stirring. The reaction continued for 2 h. The reaction mixture was cooled gradually, dispersed in acetone and the excess alkali neutralized with glacial acetic acid bringing the pH to 7. The product was finally washed with three successive portions of acetone, filtered and then dried under vacuum.

Using the aforementioned general technique, the concentration of the alkylating agent was changed to obtain derivatives having different degree of substitution (Scheme 1).




Scheme 1. Sketch (from top to bottom) of native guar gum, GG, and O-methyl-guar, MG, with degree of substitution (DS) 0.6.

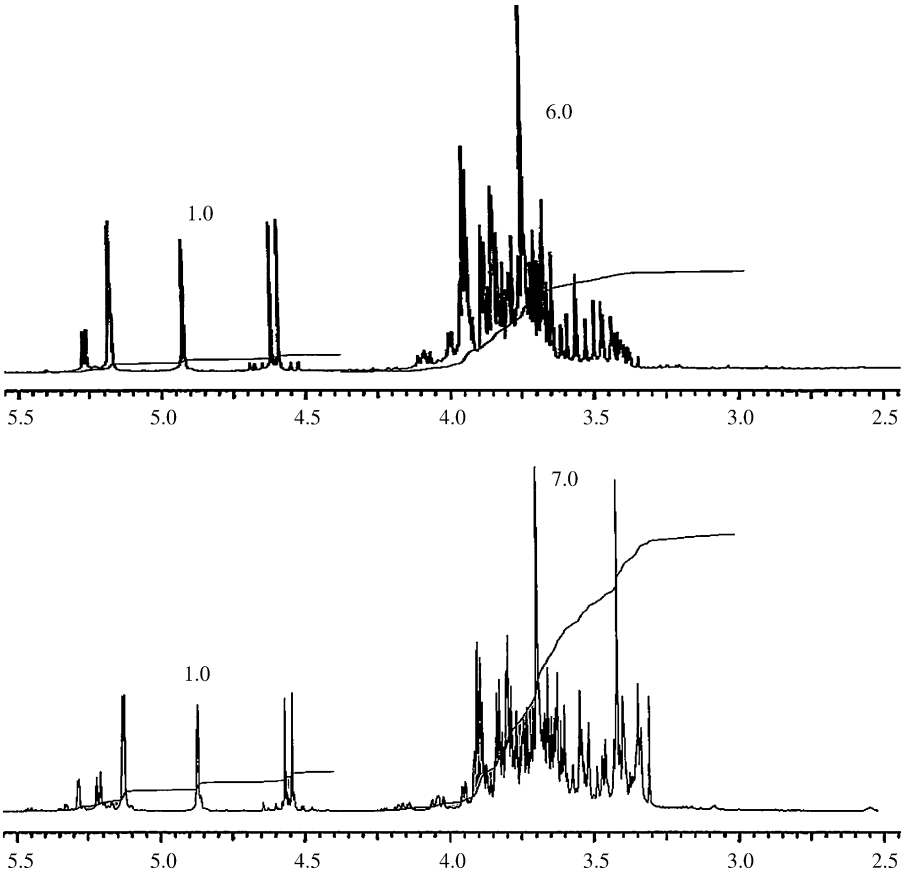



Fig. 2. $^{1}$H NMR spectra of GG (above) and MG d.s. = 0.3 (below). The bold numbers refer to the integrals of both the anomeric and non anomeric protons.

### 2.3. Purification of samples

Commercial guar gum used and the methylguar samples synthesized were purified by dissolution in deionised water, centrifugation, extensive dialysis against deionised water and lyophilisation. Crude protein content (N×5.71) for guar and MG samples was estimated, before and after purification, by the Kjeldahl method [17].

All polymer solutions were prepared by adding the proper amount of polymer to deionized water under vigorous stirring at 50 °C over-night.

### 2.4. Determination of degree of substitution (DS)

*Fourier transform infrared spectroscopy (FTIR)*: FTIR spectra of guar gum and MG have been recorded using a Shimadzu 8300 FTIR spectrometer (Shimadzu, Tokyo, Japan). One hundred and twenty-eight scans were averaged at a resolution of 4 $cm^{-1}$ with a triangle apodization. Prior to use, the spectrometer was purged with dry $N_2$. All spectra were baseline corrected and area normalized [18,19].

The sample solutions (0.25% w/v) were cast on IRTRAN crystal to obtain thin films and dried at 70 °C for 1 day. The dryness of the film was controlled by the band at ca. 1648 $cm^{-1}$, which is associated with the deformation vibrations of the OH bond of water molecules [20].

*NMR experiments*: The degree of substitution (DS) of MG samples has been controlled by means of $^{1}$H NMR measurements of completely degraded polymer samples. The latter have been prepared by dissolving 50 mg of modified guar in 0.2 mL of DCl 37% and 1 mL of $D_2O$, under stirring at 100 °C for 2 h. The solution was passed through a cotton filter directly into the NMR tube, where some crystals of TSP (3-(trimethylsilyl)-propionic-2,2,3,3-d4 acid, sodium salt, 98% D) were placed as inner reference. Spectra were recorded at 300 MHz with a Bruker AC 300P spectrometer. Each sample was measured three times.

From the $^{1}$H NMR spectra of Fig. 2 it is possible to observe that while in the case of native guar the ratio of non anomeric protons (signals at 3.2–4.4 ppm = A6) to anomeric protons (signals at 4.4–5.5 ppm = A1) is 6, as expected, in the case of MG the ratio of non anomeric (AD6) to anomeric protons gives a greater value. The elaboration of these ratios, [(AD6-A6)/A1]/3 = DS, allows to estimate the degree of substitution, DS, of methylated samples.

### 2.5. Acid degradation in dilute solution [21]

A 0.1% (w/v) solution of guar, and of two methylguar samples (MG DS = 0.3 and 0.6), respectively, were prepared. Acid hydrolysis was initiated by adjusting the solution pH to 1.0 using concentrated HCl. The solution was continuously

Table 1(a)
Formulation reference for the synthesis of MG with DST = 0.5

| Component | *g* | *n* | *R* |
|---|---|---|---|
| Guar (85% purity) | 5.88 | 0.04 | 1 |
| *t*-BuOH $d = 0.78$ (g/mL) | 10.37 | 0.14 | 3.50 |
| NaOH | 0.88 | 0.022 | 0.55 |
| $H_2O$ | 13.3 | 0.74 | 18.47 |
| DMS $d = 1.33$ (g/mL) | 2.52 | 0.02 | 0.5 |

*g*, component weight, in grams; *n*, number of moles; *R*, molar ratio component to saccaridic unit.

stirred and maintained at 70 °C in a water bath. Samples were periodically removed (0, 3, 8, 24, 32 h) and immediately neutralized to halt the degradation. GPC analysis was conducted to obtain the weight-average molecular weight ($M_w$) and polydispersity index ($I$) for all samples.

### 2.6. Viscosity measurements [22]

The viscosities of dilute aqueous solutions of GG and MG were determined using a Schott Geräte apparatus (Germany) and a Ubbelohde capillary ($\Phi = 0.53$ mm). The temperature of the thermostat was controlled within $\pm 0.1$ °C.

### 2.7. Gel permeation chromatography (GPC) measurement

The GPC system is equipped with a LabFlow 4000 HPLC pump and a Shimadzu RID-10A refractive index detector (Shimadzu, Kyoto, Japan) and two columns TSK-GEL GM-PW ($30 \times 7.5$ mm, 17 μm) in series. For protection, a guard column was used before the two columns. All columns were maintained at 40 °C to minimize peak broadening. The mobile phase was 55 mM $Na_2SO_4$ and 0.02% (w/w) $NaN_3$ with a flow rate of 0.6 ml/min. Near-monodisperse pullulan standards and a guar sample ($2 \times 10^6$ Da) were used for calibration. Degraded guar and MGs samples were diluted to 0.05% (w/v) and filtered through 0.45 μm filter prior to analysis. The injection volume was 20 μL.

## 3. Results and discussion

### 3.1. Polymer samples

The mannan:galactose ratio in purified GG, and MG samples was found to be 1.5, by $^1$H NMR measurements using totally degraded polymer samples. For both GG and MG the absence of protein material after purification has been proved by elemental analysis and infrared spectroscopy experiments.

### 3.2. Methylation

The derivatization protocol employed was designed to provide GG derivatives leading, in principle, to substitution at any hydroxyl group of the sugar rings (Scheme 1). The process is conducted in a two-phase reaction system, where the solid guar gum, derived directly from the endosperm splits without further purification, is suspended in a hydro-alcoholic mixture of isopropyl or ter-butyl alcohol. The water:alcohol ratio of the mixture solution is a very important variable, because the lower possible quantity of water should be present in the reaction medium to prevent the swelling or solubilization of the polysaccharide which would complicate product recovery and purification.

To diminish the oxidative degradation of polysaccharidic chains, the reaction systems were oxygen depleted by a combination of inert gas purging and of partial vacuum.

The etherification reaction between guar gum and alkyl reactant is conducted in the presence of a stoichiometric quantity, and most preferably a slight excess, of sodium hydroxide, which performs both as a reactant and as a catalyst (Table 1(a)). The hydroxide and the polygalactomannan gum interact to form an alkoxide derivative, which reacts with the alkylating agent through a Williamson mechanism, introducing methoxyl substituents along the polysaccharidic chains. The alkylating agents used, are dimethylsulfate (DMS) and methyliodide (MI). Both are good methylating agents, but when the etherification was carried out with the latter, for the same conditions of DMS, a small MG yield was obtained. This result may be attributed to non-homogeneity of the reaction mixture due to the lower solubility in the aqueous mixture and the higher density of MI.

The process yield is a function also of the type of alcohol used for the reaction mixture. In fact, the alkylating agent is consumed by the etherification of the polysaccharide but also by the side reaction with the alcohol in the solvent mixture. A tertiary alcohol is less reactive than a secondary one, giving a lower amount of by-products and yielding a higher degree of polysaccharide methylation (Table. 1(b)).

The chosen reaction temperature is 50 °C. In fact, different temperatures in the 40–70 °C range have been tested: the results suggest that 50 °C is the best compromise between

Table 1(b)
Theoretical, DST, and experimental, DSE, degree of substitution and reaction % yield of $-OCH_3$ subtituents induced, respectively, by MI or DMS

| Water miscible solvent | DST | DSE | | % Yield | |
|---|---|---|---|---|---|
| | | MI | DMS | MI | DMS |
| Isopropanol | 1.00 | 0.16 | 0.25 | 16.00 | 25.00 |
| | 2.00 | 0.40 | 0.60 | 20.00 | 30.00 |
| Ter-butanol | 0.50 | 0.10 | 0.30 | 20.00 | 60.00 |
| | 2.00 | 0.60 | 1.70 | 30.00 | 85.00 |

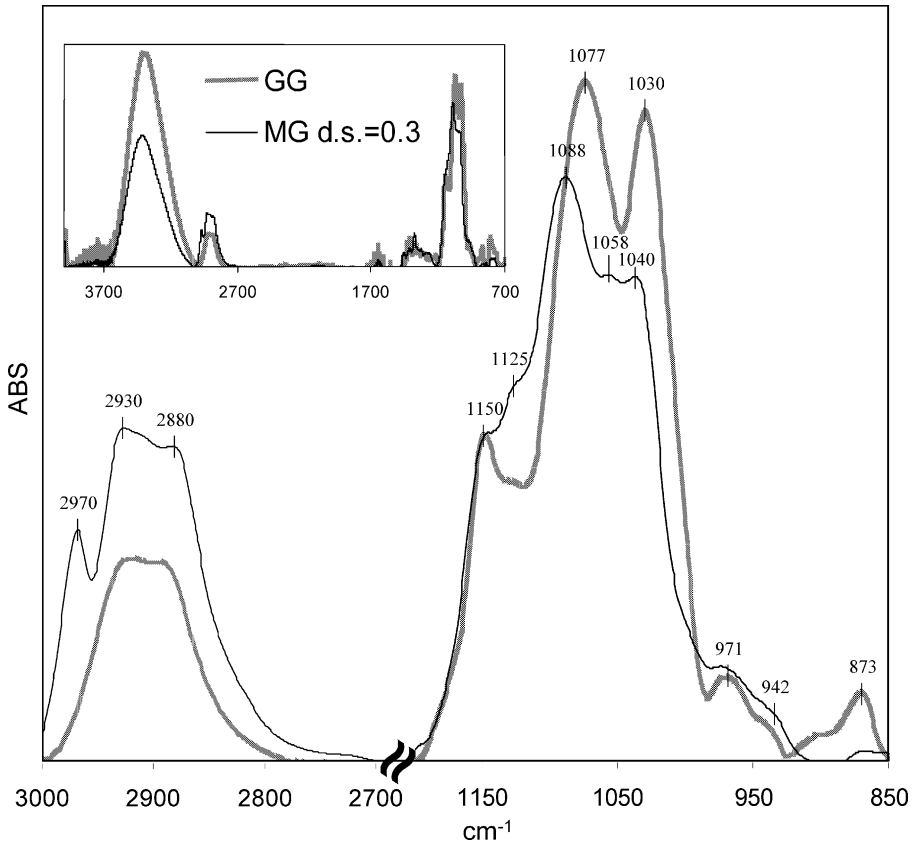



Fig. 3. Infrared spectra of films of GG and MG d.s. = 0.3 samples at the frequencies between 3000–2700 and 1200–850 $cm^{-1}$. The complete range of frequencies between 4000 and 700 $cm^{-1}$ is shown in the insert.

reaction rate and chains depolymerization. In heterogeneous phase to obtain the same DS, the alkylating agent:guar gum ratio is usually greater than that used in homogeneous reactions, because the galactomannan molecules are not isolated but packed into aggregates [23–25]. These aggregates are difficult to penetrate by reagents so the methylation of guar galactomannan in heterogeneous phase produces patterns of substitution, which do not depend on the relative reactivity of the hydroxyl groups, but are governed by the state of aggregation of the polysaccharide. Quite naturally, increasing the amount of alkylating agent increases the degree of substitution. However, to maximize the final DS it would be necessary to increase the sodium hydroxyde concentration which could lead to extensive chains cleavage and hence to a reduction in molecular weight.

Temperature is another very important variable for the optimization of the process. At relatively high temperatures the reaction is faster but the formation of by-products increases: the etherification process has, therefore, been carried out at normal pressure and not high temperature (40 °C for DMS and 30 °C for MI) which also allows a safer handling of hazardous reagents. The boiling temperature of MI is lower than that of DMS so it is necessary to work at a lower reaction temperature in order to diminish the loss of alkylating agent during the reaction period. By the term 'degree of substitution' is meant the number of moles of ether groups per anhydro sugar unit. Employing the method explained above, we have obtained derivatives with degree of substitution ranging between 0.1 and 1.7.

Aqueous solutions of MG exhibit excellent heat stability and have a greater clarity and stability under extreme conditions of pH and in the presence of polyvalent metal ions than GG solutions.

### 3.3. Fourier transform infrared spectroscopy (FTIR)

In Fig. 3 the infrared film spectra of native and methylated guar gum with degree of substitution 0.3 are shown. In the native guar spectrum the band at 3200–3600 $cm^{-1}$ is shifted to lower frequencies and is more asymmetric and narrower than for the MG sample, suggesting the formation of stronger hydrogen bonds. This can be attributed to methyl substitution along the polysaccharide chain, which leads to a significant change in the intra- and inter- molecular hydrogen bonding array prevailing with pure GG. In the IR spectrum of MG DS = 0.3 moreover there are absorption bands at 2970, 2930, 2880 $cm^{-1}$ and at 942 $cm^{-1}$ characteristic of stretching and bending modes of the C–H group of methyl ether moieties [26]. Analysis of FTIR data show that each particular polysaccharide has a specific band maximum in the 1200–900 $cm^{-1}$ region [18]. The band at about 1150 $cm^{-1}$ has been previously

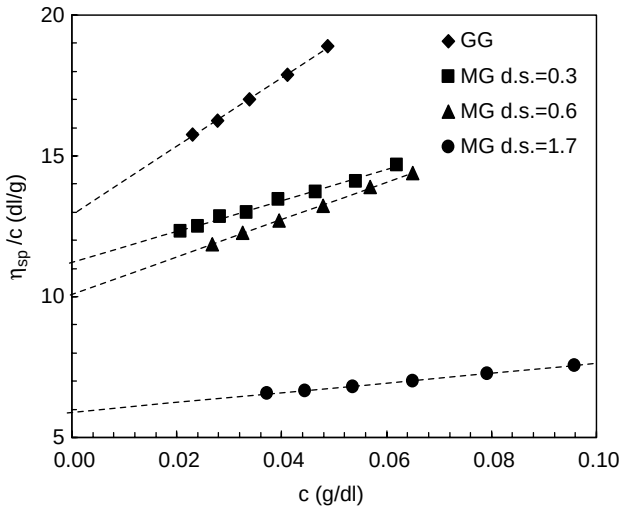



Fig. 4. Reduced specific viscosity at 25 °C of aqueous GG and MG solutions at different DS.

assigned to vibrations of the C–O–C bonds of glycosidic bridges: in fact, this band is evident in our IR spectra.

Complex vibrations involving the stretching of the $C_6$–O–$C_1$ bonds linking the galactose residue to the main chain (with participation of the $C_4$–$C_5$ bonds vibrations) result in the appearance of the band at 1077 $cm^{-1}$ in the native guar spectrum. This band is slightly shifted to higher frequencies (1088 $cm^{-1}$) for MG DS = 0.3. In the guar structure there is a larger proportion of primary alcoholic groups because a portion of such groups is methyl etherified in MG. Just this substitution causes the reduction of band intensity at 1080 $cm^{-1}$ as it is shown in MG spectrum [19]. The band at 1030 $cm^{-1}$ is relative to stretching (C–O) of the alcoholic groups [27]: the substantial reduction of this band in the MG spectrum thus confirms the formation of ether bonds, consistent with the two bands at 1125 and 1058 $cm^{-1}$ typical of asymmetric ether bond stretching.

### 3.4. Intrinsic viscosity and the effect of methyl substitution

Fig. 4 shows the Huggins plots for native guar and MGs at 25 °C. The calculated intrinsic viscosity [$\eta$] and Huggins coefficients values ($K_H$) at 25 °C and 40 °C are listed in Table 2. Kraemer plots were also drawn, and similar results of calculated intrinsic viscosity (not reported in the figure) were obtained. The Huggins coefficient should be independent of $M_w$ for long chains, with values of roughly 0.30–0.40 in good solvents and 0.50–0.80 in $\theta$ or bad solvents. The Huggins coefficient is a measure of polymer–polymer interactions in solution, thus when intermolecular association exists, the Huggins coefficient increases [28]. At 25 °C natural guar has an intrinsic viscosity of 13.8 dL/g and Huggins coefficient of 1, higher than any of the MG samples. Water is a fairly good solvent for guar. However, its Huggins coefficient in water indicates the importance of polymer–polymer hydrogen bonding interactions. The aggregation is an intrinsic property of native guar. It has been reported that guar is highly prone to form hydrogen-bonded complexes both inter- and intramolecular through the unsubstituted region on its backbone [29]. When the methyl groups are added to guar, the substitution occurs at any of the hydroxyl groups on the chain, on the backbone or on the galactose side groups. This heterogeneous substitution of methyl groups sterically blocks the hydrogen bonding sites on the guar backbone reducing the inter and intramolecular hydrogen bonds, respectively, between polymer molecules and, along a single chain, between adjacent residues.

In Table 2 are reported the Huggins coefficients as a function of methyl substitution at 25 and 40 °C. At both temperatures $K_H$ at first drops with DS, until DS = 0.3, then becomes independent of DS. This trend suggests two regimes of behaviour: only in the first there would be a sharp decrease in intermolecular interactions.

The average molecular weight of guar and MGs has been determinate by GPC analysis (listed in Table 3): the molecular weights of the samples decrease proportionally with substitution. Combined with the intrinsic viscosity results, through the Flory–Fox equation [30], the effective molecular volume of polymer coils, $[\eta]M_w/\phi$, is reported for different substitution degrees (assuming a $\phi$ value equal to $2.5\times10^{23}$ $g^{-1}$) in Table 2. Guar exhibits a highest value of molecular volume, because, as already mentioned above, methyl substitution reduces the inter and intra molecular attractions decreasing both the effective molecular volume and the local chain rigidity.

### 3.5. Mark–Houwink–Sakurada (MHS) relationships for GG and MG

MG DS = 0.3, MG DS = 0.6 and guar have been degraded using the acid hydrolysis procedure described in the

Table 2
Intrinsic viscosity, [$\eta$], Huggins coefficient, $K_H$, and molecular volume, for GG and MG derivatives at 25 and 40 °C

| | At 25 °C | | At 40 °C | | |
|---|---|---|---|---|---|
| | [$\eta$] (dl/g) | $K_H$ | [$\eta$] (dl/g) | $K_H$ | Molecular volume $\times10^{20}$ (dl/molecule) |
| GG | 13.8 | 1 | 11.4 | 0.7 | 13.7 |
| MG DS = 0.3 | 11.2 | 0.4 | 8.0 | 0.6 | 7.2 |
| MG DS = 0.6 | 10.2 | 0.6 | 9.5 | 0.6 | 9.3 |
| MG DS = 1.7 | 5.9 | 0.5 | 5.3 | 0.6 | – |

Table 3
Intrinsic viscosity, [$\eta$], Huggins coefficient, $K_H$, weight average molecular weight, $M_w$, number average molecular weight, $M_n$ and polydispersity index, $I$ for GG and MG degraded samples at different time of hydrolysis

| Sample | Hydrolysis $t(h)$ | [$\eta$] (dl/g) | $K_H$ | $M_w\times10^{-6}$ (g/mol) | $M_n\times10^{-6}$ (g/mol) | $I$ |
|---|---|---|---|---|---|---|
| Guar | 0 | 11.4 | 0.7 | 2.7 | 1.4 | 1.9 |
| | 3 | 9.4 | 0.7 | 1.5 | 0.8 | 2.0 |
| | 8 | 7.2 | 0.5 | 1.3 | 0.6 | 2.0 |
| | 24 | 5.2 | 0.7 | 0.8 | 0.4 | 2.2 |
| | 32 | 4.1 | 0.8 | 0.6 | 0.3 | 2.2 |
| MG DS=0.3 | 0 | 7.8 | 0.6 | 2.7 | 1.5 | 1.8 |
| | 4 | 6.4 | 0.6 | 1.9 | 1.0 | 1.9 |
| | 7 | 5.4 | 0.6 | 1.7 | 0.7 | 2.3 |
| | 32 | 1.9 | 0.7 | 0.4 | 0.2 | 2.1 |
| MG DS=0.6 | 0 | 8.8 | 0.5 | 2.1 | 1.1 | 2 |
| | 4 | 5.5 | 0.5 | 1.2 | 0.5 | 2.2 |
| | 7 | 4.8 | 0.6 | 1.0 | 0.4 | 2.3 |
| | 24 | 4.8 | 0.5 | 0.4 | 0.2 | 2.3 |

Experimental part. The number average molecular weight ($M_n$), weight average molecular weight ($M_w$), and the polydispersity index ($I=M_w/M_n$) of degraded polymers were determined by GPC. The degradation process produces samples with a rather uniform molecular weight distribution: the polydispersity does not change significantly for different degraded samples, with an average value between 1.8 and 2.3.

Intrinsic viscosity, [$\eta$], is related to the viscosity average $M_w$ of the polymer through the Mark–Houwink–Sakurada (MHS) relationship: $[\eta]=KM^{\alpha}$, where $K$ and $\alpha$ are constants, both related to the stiffness of the chains. For flexible polymer coils, $\alpha$ varies between 0.5 and 0.8 (0.5 in $\theta$ solvent and 0.8 in good solvent), whereas it increases with increasing chain stiffness up to 1.8 for rigid rod. The MHS relationship can be determined by using degraded samples with various $M_w$ but with random (Flory) $M_w$ distribution, thus we can assume the approximation: $M_w\approx M_v$ [31–33].

$M_w$ determination by GPC is based on a universal calibration curve and the MHS relationship reported from literature. For this analysis four degraded samples of guar gum have been selected and also two set of four degraded MGs with DS=0.3 and 0.6, thus their intrinsic viscosity were measured.

The GPC data for the degraded MG samples were analyzed using, for the first iteration, the MHS parameters of natural guar and were then reported as a double log plot of intrinsic viscosity against $M_w$ (Fig. 5). These data give, respectively, the following MHS parameters: $K=3.60\times10^{-4}$ and $\alpha=0.714$, for guar; $K=1.93\times10^{-4}$ and $\alpha=0.739$, for MG DS=0.3 and $K=1.91\times10^{-4}$ and $\alpha=0.750$, for MG DS=0.6. Then the molecular weight was recalculated using the experimental MHS values obtained by means of MGs plot. The iterative process of calculating molecular weight, determining the MHS parameters, and then resolving for the molecular weights were repeated until identical results, within experimental error, were obtained (Table 3). This iteration procedure permits to obtain MHS relationship of all samples analysed reported in Table 4. For guar gum these values are in good agreement with those provided in the literature [31]. As regards MG samples, the exponents are within the range of 0.5–0.8. The slight increase

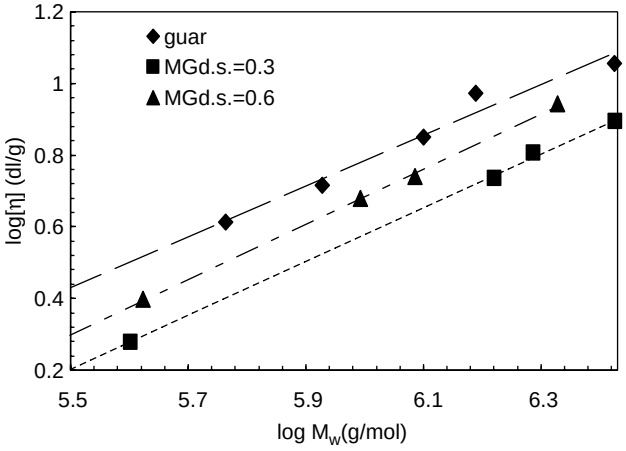



Fig. 5. The relationship between intrinsic viscosity, [$\eta$] and molecular weight, $M_w$ for GG, and MG DS=0.3 and 0.6, respectively, is shown as a double-log Mark–Houwink–Sakurada plot.

of these values for MG may be a symptom of lesser thermodynamically favourable polymer-water interactions with respect to GG.

### 3.6. The Burchard–Stockmayer–Fixman method, characteristic ratio ($C_\infty$) and chain persistence length ($L_p$)

The Burchard–Stockmayer–Fixman (BSF) equation permits-through an extrapolation to estimate the unperturbed coil dimensions from the perturbed ones, on condition that the intrinsic viscosity of the polymer under scrutiny is known for a wide range of molecular weights.

Table 4
MHS constants, $\alpha$ and $K$, characteristic ratio, $C_\infty$, and persistence length, $L_p$, for GG and MG DS=0.3 and 0.6 samples

| | $\alpha$ | $K$ ($\times10^4$) | $C_\infty\pm1.2$ | $L_p\pm1.3$ |
|---|---|---|---|---|
| Guar | 0.71 | 3.38 | 12.4 | 3.3 |
| MG DS=0.3 | 0.75 | 1.18 | 7.7 | 2 |
| MG DS=0.6 | 0.77 | 1.20 | 8.6 | 2.3 |

Table 5
Intrinsic viscosity, [$\eta$], and Huggins coefficient, $K_H$, for GG and MG with degree of substitution (DS) 0.3 and 0.6, at different temperature

| $T$ (°C) | GG | | MG DS = 0.3 | | MG DS = 0.6 | |
|---|---|---|---|---|---|---|
| | [$\eta$] (dl/g) | $K_H$ | [$\eta$] (dl/g) | $K_H$ | [$\eta$] (dl/g) | $K_H$ |
| 25 | 13.8 | 1 | 11.2 | 0.4 | 10.2 | 0.7 |
| 30 | 12.7 | 0.7 | 10.6 | 0.5 | 9.7 | 0.7 |
| 40 | 11.4 | 1 | 8.0 | 0.6 | 9.5 | 0.6 |
| 50 | 9.0 | 0.3 | 8.9 | 0.7 | 8.8 | 0.6 |

The Burchard–Stockmayer–Fixman equation is defined as: $[\eta]/M_w^{1/2} = K_\theta + 0.51\phi B M_w^{1/2}$ where the slope is a measure of the long-range interactions, and the intercept of the plot, $K_\theta$, which corresponds to a polymeric chain in the $\theta$-state, where there is no excluded volume, is proportional to the characteristic ratio $C_\infty$ according to $K_\theta = \phi l^3/(C_\infty/m_0)^{3/2}$ in which $m_0$ and l represents the $M_w$ and length of one monomeric unit and $\phi$ is the Flory's universal constant.

The characteristic ratio $C_\infty$ is a measure of the degree of directional correlation between neighbouring residues and hence of the stiffness of a real chain. In Fig. 6 the Stockmayer–Fixman plots for guar and MGs with DS = 0.3 and 0.6 are shown. The intercepts of the plots give characteristic ratio values for all samples which are reported in Table 4, assuming l = 0.54 nm and $m_0$ = 270 for guar, 277.5 for MG DS = 0.3 and 285 for MG DS = 0.6.

In the wormlike chain approximation the characteristic ratio is simply equal to $2L_p/l$. We can then obtain the values of persistence length ($L_p$) for all samples (Table 4). These values agree quite well with the earlier tabulated values of $L_p$ for guar [31], cellulose derivatives [34] and xyloglucans [35]. The overall difference between values obtained for MG samples is within experimental error.

The value of $C_\infty$ obtained for native guar is in good agreement with previous results determined by light scattering and viscosity measurement reported in the literature [31]. For both MG samples the $C_\infty$ value is lower than that obtained for native guar according to the expectations [36] based on experimental solution data collected at 25 °C presented in the previous sections.

### 3.7. Effect of temperature on the intrinsic viscosity of guar and its derivatives

The effect of temperature on the intrinsic viscosity of guar and MG samples with DS = 0.3 and 0.6 in aqueous solution has been studied and the results are reported in Table 5. Fig. 7 is the plot of (ln[$\eta$]) versus the inverse of absolute temperature ($1/T$ $K^{-1}$) for GG and MG derivatives. The slopes (dln[$\eta$]/d($1/T$)) were obtained by regression analysis and are listed in the insert of Fig. 7: these values decrease with increasing degree of substitution, showing that the chain flexibility of methylated samples is greater than for guar gum [37–39]. Between 25 and 50 °C, the intrinsic viscosity decreases with increasing solution temperature, but only for MG DS = 0.3 and 0.6 it decreases linearly. For GG there results a more complex temperature-dependent rheological behaviour traceable to a gradual collapse of hydrogen bonded chains ensembles.

## 4. Conclusions

An improved process for the etherification of guar gum flour, carried out in heterogeneous phase, leads to a new non-ionic hydrocolloid (MG) with interesting properties with

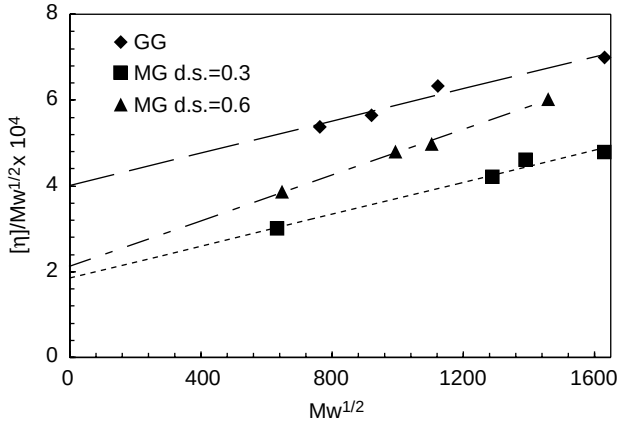



Fig. 6. The Stockmayer–Fixman plot of GG, and MG at DS = 0.3 and 0.6, respectively, to determine the characteristic ratio. The intercept represents local conformational constraints of the polymer. The slope is a measure of the long-range interactions.

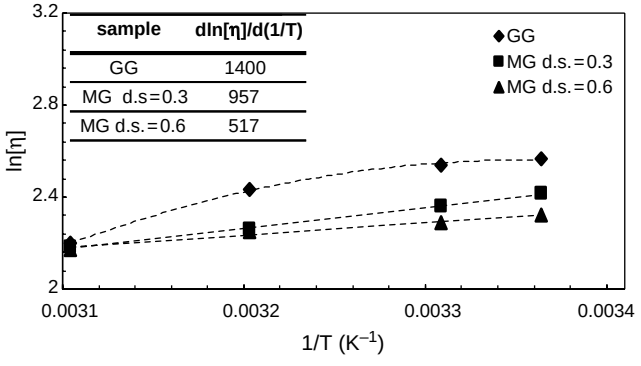



Fig. 7. Plot of natural logarithmic intrinsic viscosity (ln[$\eta$]) versus the inverse of absolute temperature ($1/T$, $K^{-1}$) of GG and MG at DS = 0.3 and 0.6, respectively, in aqueous solution. The slopes dln[$\eta$]/d($1/T$) of linear behavior are reported in the insert.

respect to the native biopolymer. This shows up in a distinctly higher solubility in aqueous media and higher chain flexibility. Such differences between guar gum and MG are traceable primarily to a partial suppression of inter and intra molecular hydrogen bonds caused by methoxyl substitutions.

The dependence of viscosity on temperature and DS shows that a degree of substitution 0.3 is sufficient to markedly reduce interactions between guar chains. A comparative analysis of Mark–Houwink–Sakurada parameters and of the characteristic ratio $C_\infty$, estimated by the BSH plots, suggests that all samples considered behave as linear flexible/semiflexible coiled carbohydrate polymers and shows that MG samples exhibit a higher flexibility than native guar.

These conclusions will be further scrutinized in a forthcoming paper dealing with light scattering and diluite and semidiluite solution rheology of GG and MG.

## Acknowledgements

Financial support of this work by Lamberti S.p.A, Albizzate, Italy is gratefully acknowledged.

## References

[1] McCleary BV, Clark AH, Dea ICM, Rees DA. Carbohydr Res 1985;31:241–312.
[2] Prud'homme RK, Constien V, Knoll S. Adv Chem Ser 1989;223:89–112.
[3] Cheng Y, Prud'homme RK. Biomacromolecules 2000;1:782–8.
[4] Fox JE. In: Imeson A, editor. Thickening and gelling agents for food. New York: Blackie Academic Professional; 1997. p. 262.
[5] Whistler RL, BeMiller JN. Industrial gums: polysaccharides and their derivatives. San Diego, CA: Academic Press; 1993.
[6] Brode GL, Goddard ED, Harris WC, Salensky GA. In: Gebelein CG, Cheng TC, Yang VC, editors. Cosmetic and pharmaceutical applications of polymers. New York: Plenum Press; 1991. p. 117–28.
[7] Goyocoolea FM, Morris ER, Gidley MJ. Carbohydr Polym 1995;27:69–71.
[8] Cheng Y, Prud'homme RK. Macromolecules 2002;31:10155–101661.
[9] Chattrji J, Borchardt JKJ. J Pet Technol 1981;33:2042.
[10] Denham WS, Woodhaouse HJ. Chem Soc 1913;103:1735–42.
[11] Haworth WN. J Chem Soc 1915;107:8–12.
[12] Srivastava HC, Harche SN. Tetrahedron Lett 1963;27:1869–73.
[13] Hakamori J. Biochem (Tokyo) 1964;55:205–8.
[14] Hough L, Theobald RS. Methods Carbohydr Chem 1963;2:162–6.
[15] Singh V, Tiwari A, Tripathi DN, Malviya T. Tetrahedron Lett 2003;44:7295–7.
[16] Manzi AE, Cerezo AS. Carbohydr Polym 1986;6:349–50.
[17] Kirk RS, Sawyer R. Pearson's chemical analysis of foods. UK: Longman Group UK Ltd; 1991 p. 8–42.
[18] Kačuráková M, Capek P, Sasinková V, Wellner N, Ebringerová A. Carbohydr Polym 2000;43:195–203.
[19] Shingel KI. Carbohydr Res 2002;337:1445–51.
[20] Bellamy LJ. The infrared spectra of complex molecules. London: Methuen; 1954.
[21] Cheng Y, Brown KM, Prud'homme RK. Biomacromolecules 2002;3:456–61.
[22] Young RJ, Lovell PA. Introduction of polymes. 2nd ed. New York: Chapman & Hall; 1991.
[23] Palmer KJ, Ballantyne MJ. Am Chem Soc 1950;72:736–41.
[24] Aisenberg E, Smolko EE, Serezo AS. An Asoc Quim Aegent 1974;62:113.
[25] Warwicker JO, Wright A. J Appl Polym Sci 1967;11:659–71.
[26] Kutseuko LI, Ivanova NP, Karetnikova EB, Bobasheva AS, Bochek AM, Panarin EF. Russ J Appl Chem 2002;75:305–9.
[27] Kačuráková V, Wellner N, Ebringerová A, Hromadkova Z, Wilson RH, Belton PS. Food Hydrocoloids 1999;13:35–41.
[28] Bohdanecky M, Kovar J. Viscosity of polymer solutions. Amsterdem: Elsevier; 1982.
[29] Morris ER, Cutler AN, Ross-Murphy SB, Ress DA. Carbohydr Polym 1981;1:5–21.
[30] Flory PJ. Principles of polymer chemistry. New York: Cornell University Press; 1953.
[31] Robinson G, Ross-Murphy SB, Morris ER. Carbohydr Res 1982;107:17.
[32] Cheng Y, Brown KM, Prud'homme RK. Int J Biol Macromol 2002;31:29–35.
[33] Picout DR, Ross-Murphy SB, Errington N, Harding SE. Biomacromolecules 2001;2:1301–9.
[34] Ross-Murphy SB. In: Nevell TP, Zeronian SH, editors. Cellulose chemistry and its applications. Chichester, UK: Ellis Horwood Ltd; 1985. p. 202.
[35] Yilong R, Picout DR, Ellis PR, Ross-Murphy SB. Biomacromolecules 2004;5:2384–91.
[36] Jinping Z, Lina Z, Jie C. J Polym Sci, Part B: Polym Phys 2004;42:347–53.
[37] Chem RH, Tsaih ML. Int J Biol Macromol 1998;23:135–41.
[38] Launay B, Doublier JL, Cuvelier G. In: Mitchell JR, Ledward DA, editors. Functional properties of food macromolecules. London: Elsevier Applied Science; 1986. p. 1–78.
[39] Noguchi H. In: Rockland LB, Stewart GF, editors. Water activity: influences on food quality. New York: Academic Press; 1981. p. 281–93.