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

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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_∞) 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_∞, of GG and MG derivatives have been evaluated. The dependence of intrinsic viscosity on temperature has been

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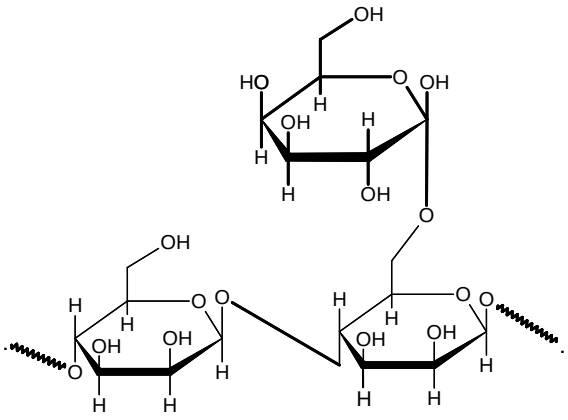


Fig. 1. Structure of guar gum (GG): guar gum has a linear backbone of β-1,4-linked mannose units with α-1,6-linked galactose units attached as side chains.

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

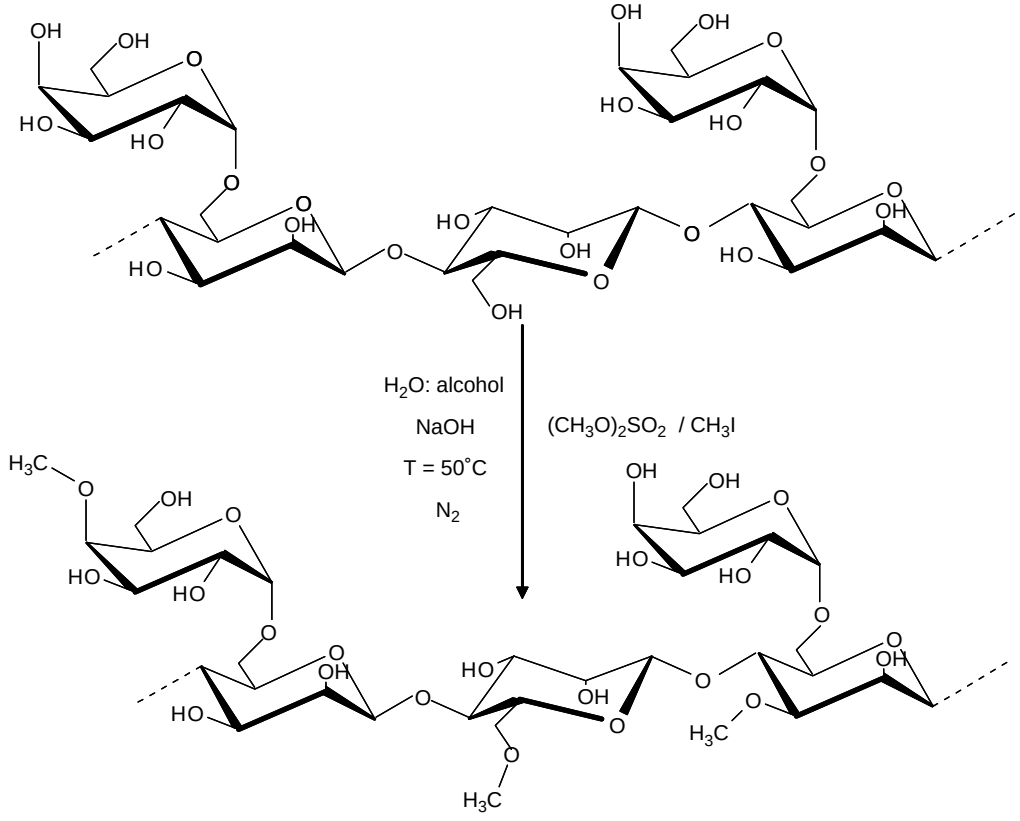
2.1. Materials

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.