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Description of Heteropolysaccharide Ethers: Hydroxypropyl Guar and Carboxymethyl Guar

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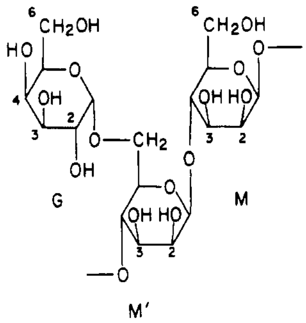
ABSTRACT: A statistical kinetic model for the description of heteropolysaccharide ethers is presented. According to the model, for the description of such polymers, one needs the mole fractions of the component monosaccharide types and the relative rate constants of reaction of the hydroxyls. The necessary information can be extracted from the monomer composition. It is shown that the model affords an excellent description of analytical data on hydroxypropyl guar and carboxymethyl guar. In guar the primary hydroxyls at position 6 of both the mannose and galactose units are preferred in the hydroxypropylation reaction, whereas position 2 of mannose exhibits a slight preference in the carboxymethylation process.

Introduction

Guar gum and its derivatives are among the most important water-soluble polymers. Major uses are in the oil, textile, paper, food, explosives, and mining industries.[1]

Guar is a galactomannan composed of 1→4 β-linked mannopyranosyl residues with galactopyranosyl side chains attached at (approximately) every other mannopyranosyl unit in a 1→6 α-linkage. Upon ether formation and at low degrees of substitution, some of the hydroxyl groups are substituted, leading to a polymer composed of many different monomers. The hydroxyls available for reaction are at positions 2, 3, 4, and 6 of the galactose (G) residues, positions 2, 3, and 6 of the mannose (M) residues, and positions 2 and 3 of the mannose residues that bear a galactose (M′). Thus, even at low levels of substitution, where only unsubstituted, monosubstituted, and disubstituted residues have to be considered, the polymer is composed of 22 monomers of different abundancies. The description and characterization of a polymer of such complexity are challenging problems. Recently, the formidable analytical tasks of determining the monomer compositions of hydroxypropyl guar and carboxymethyl guar have been accomplished.[2,3]



This article presents a mathematical framework for the description of heteropolysaccharide ethers and for the treatment and interpretation of analytical data. The approach is an extension of the statistical models[4] used for the description of cellulose derivatives.[5-7]

Theory

The model used in this work is similar to the ones used for the description of cellulose ethers.[4,6] It involves the following assumptions: (a) All monosaccharide units of the polymer are equally accessible for reaction. (b) The relative rate constants of reaction of the hydroxyls remain unchanged throughout the process. (c) Substitution within a given unit does not affect the reactivity of the remaining hydroxyls. (d) The effects of end groups are negligible.

Thus, for any given position j of monosaccharide unit I one can write the reaction

$$\underset{p_{Ij}}{-C_{Ij}-OH} + RX \xrightarrow{k_{Ij}} -C_{Ij}-OR + HX \tag{1}$$

where k_{Ij} is the relative first-order rate constant of reaction of the hydroxyl at position j of monosaccharide I and p_{Ij} is the mole fraction of such unsubstituted hydroxyls. The latter will decay exponentially with increasing substitution level

$$p_{Ij} = W_I e^{-Bk_{Ij}} \tag{2}$$

where W_I is the mole fraction (or probability of occurrence) of the monosaccharide residue of type I (for guar I can be G, M, or M′ and $W_G = W_{M'}$) and B is a factor with the dimension of time. The probability of having a substituent at position j of monosaccharide I is thus given by

$$X_{Ij} = W_I - p_{Ij} = W_I(1 - e^{-Bk_{Ij}}) \tag{3}$$

The latter can be determined experimentally from the mole fractions S_{Ij} of monosaccharide I substituted at position j; viz.

$$X_{Ij} = \sum_j S_{Ij} \tag{4}$$

Note that, since multiple substitutions are possible, the index j in S_{Ij} may take values such as 23, 26, etc., in addition to 2, 3, etc. The mole fraction of unsubstituted monosaccharide of type I will be denoted by S_{I0}. The probability of having unsubstituted units of type I is given by the product

$$S_{I0} = W_I \prod_j e^{-Bk_{Ij}} \tag{5}$$

The probability of having a unit of type I substituted only at position j is

$$S_{Ij} = W_I(1 - e^{-Bk_{Ij}}) \prod_{l \neq j} e^{-Bk_{Il}} \tag{6}$$

Similarly, for double substitution, one has

$$S_{Ij} = W_I(1 - e^{-Bk_{Ij}})(1 - e^{-Bk_{Il}}) \prod_{m \neq j \neq l} e^{-Bk_{Im}} \tag{7}$$

The total (average) degree of substitution is

$$D = \sum_I \sum_j X_{Ij} = \sum_I \sum_j S_{Ij} \tag{8}$$

Thus, in order to describe a heteropolysaccharide ether of degree of substitution D one needs the mole fractions, W_I, of the component monosaccharides and the complete set of relative rate constants k_{Ij}. The latter can be extracted from analytical data as shown in the next section.

Data Analysis

McNeil et al. have published complete monomer analyses of hydroxypropyl guar[2] and carboxymethyl guar.[3] For the purpose of this work their triplicate data were averaged and the mole fractions of unsubstituted residues were

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Table I
Monomer Compositions (mol %) of Hydroxypropyl Guar and Carboxymethyl Guar

monomer	HP-guar[a]	CM-guar[b]	monomer	HP-guar[a]	CM-guar[b]
S_{G0}	21.03	16.29	S_{M0}	15.0	13.0
S_{G2}	2.2	3.7	S_{M2}	3.1	5.7
S_{G3}	2.6	3.1	S_{M3}	1.7	1.4
S_{G4}	0.9	3.4	S_{M6}	5.2	5.1
S_{G6}	6.8	4.5	S_{M23}	0.4	0.58
S_{G23}	0.2	0.6	S_{M26}	1.1	1.6
S_{G24}	0.11	0.6	S_{M36}	0.7	0.42
S_{G26}	0.8	1.3	$S_{M'0}$	27.0	23.92
S_{G34}	0.16	0.5	$S_{M'2}$	6.0	8.6
S_{G36}	0.9	1.4	$S_{M'3}$	2.8	2.6
S_{G46}	0.4	0.71	$S_{M'23}$	0.6	0.98

[a] Averaged and adjusted (see text) from the data in ref 2; $D = 0.42$. [b] Average and adjusted (see text) from the data in ref 3; $D = 0.55$.

Table II
Relative Rate Constants of Hydroxypropylation and Carboxymethylation of Guar

	HP-guar	CM-guar
W_G, mol %	36.4	36.1
k_{G2}	2.17	1.21
k_{G3}	2.55	1.08
k_{G4}	[1.00]	[1.00]
k_{G6}	6.39	1.59
W_M, mol %	27.2	27.8
k_{M2}	4.21	2.14
k_{M3}	2.47	0.58
k_{M6}	6.76	1.90
$W_{M'}$, mol %	36.4	36.1
$k_{M'2}$	4.54	1.98
$k_{M'3}$	2.22	0.67

Table III
Conformity of Guar Derivatives to the Model: Parameters of Regression Analysis according to Eq 11

parameter	HP-guar	CM-guar
a, mol %	−0.011 44	−0.031 40
b	1.002 72	0.998 11
r	0.999 94	0.999 14

adjusted in order to have $W_G = W_{M'}$, as expected for guar. Also, after a preliminary analysis of the data, the values for the hydroxypropyl derivatives S_{G23} and $S_{M'23}$ given in Table II of ref 2 were interchanged in order to agree with the chromatogram published in that reference and a number of overlaps (coelutions) were resolved (vide infra). The results are summarized in Table I.

The first step in the data analysis is the calculation of the mole fractions of the monosaccharide types

$$W_I = \sum_I S_{Ij} \tag{9}$$

Then, after the values of X_{Ij} are calculated with eq 4, eq 3 is solved for Bk_{Ij}

$$Bk_{Ij} = -\ln (1 - X_{Ij}/W_I) \tag{10}$$

The relative rate constants can be obtained by assuming, e.g., $k_{G4} = 1.0$ and computing Bk_{Ij}/Bk_{G4}. The results obtained are summarized in Table II. One can now use these results to calculate the expected values for each of the monomers,[8] thereby testing the conformity of the polymer to the model. The results obtained for HP-guar are shown in Figure 1 and those for CM-guar are shown in Figure 2. As seen, both materials conform to the model very well. The results of the regression analysis according to

$$S_{\text{exptl}} = a + bS_{\text{calcd}} \tag{11}$$

with the mole fractions given in mol %, are summarized in Table III. The excellent conformity is indicated by all three parameters: correlation coefficients (r) and slopes (b) close to unity and negligibly small intercepts (a).

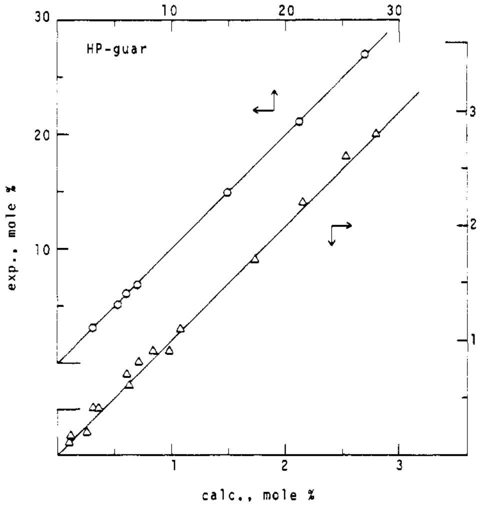

Figure 1. Plot of experimental vs. calculated mole fractions of the monomers of hydroxypropyl guar: circles (upper frame) indicate values >3 mol %; triangles (lower frame) indicate values <3 mol %. The lines describe ideal behavior: intercept of zero and slope of unity. The results of linear regression analysis are given in Table III.

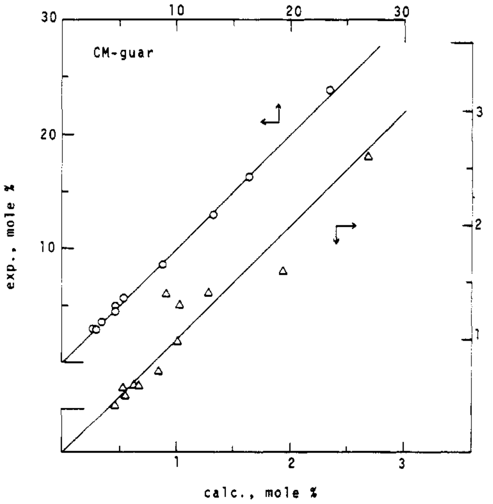

Figure 2. Plot of experimental vs. calculated mole fractions of the monomers of carboxymethyl guar: circles (upper frame) indicate values >3 mol %; triangles (lower frame) indicate values <3 mol %. The lines describe ideal behavior: intercept of zero and slope of unity. The results of linear regression analysis are given in Table III.

Discussion

Hydroxypropyl guar and carboxymethyl guar can be described by a simple statistical model. According to this model a complete description of a heteropolysaccharide ether requires the mole fractions of the monosaccharide types comprising the original polymer and a set of relative rate constants of reaction of the hydroxyls. There is a degree of chemical selectivity in the reactivity of the different hydroxyls of guar (see Table II). The primary hydroxyls at positions 6 of mannose and galactose are preferred in the hydroxypropylation reaction, the sequence being $k_{M6} \simeq k_{G6} > k_{M'2} \simeq k_{M2} > k_{G3} \simeq k_{M3} \simeq k_{M'3} \simeq k_{G2} > k_{G4}$. On the other hand, in the carboxymethylation reaction there is a slight preference for position 2 of mannose, the sequence being $k_{M2} \simeq k_{M'2} \simeq k_{M6} > k_{G6} > k_{G2} > k_{G3} \simeq k_{G4} > k_{M'3} \simeq k_{M3}$. Similar trends can be observed in comparing (hydroxyethyl)cellulose[6] and (carboxymethyl)cellulose.[5] Note that the involvement of carbon 6 of mannose in the glycosidic linkage with galactose has only a minor influence on the relative reactivities of the hydroxyls at positions 2 and 3. Thus, the assumption that substitution within a given unit does not affect the reactivity of the remaining hydroxyls receives independent support.

References and Notes

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(8) Also, these expectation values provide a mathematical means of resolving pairs of monomers that could not be separated chromatographically.

Structural Changes in Polystyrene–Polybutadiene–Polystyrene Block Polymers Caused by Annealing in Highly Oriented State

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ABSTRACT: The effect of annealing on morphological changes of highly oriented SBS block polymers was studied by small-angle X-ray scattering techniques. The SBS block polymer specimens studied had a morphology of cylindrical microdomains of polystyrene (PS) in a matrix of polybutadiene in the undeformed state. They were deformed initially to a draw ratio of $\lambda_0 = 6$ and then annealed at constant dimensions at various temperatures between 50 and 250 °C. Depending on the annealing temperature T_a, various morphological changes were observed: (i) at $T_a < T_g$ (the glass transition temperature of PS), the resultant morphology was influenced by both nonrecoverable reorientation of the microdomains and elastically recoverable orientation; (ii) at $T_g < T_a < T_c$ (order–disorder transition of the block polymer), well-oriented microdomain morphology was formed by nonrecoverable reorientation of polystyrene microdomain; and (iii) at $T_a > T_c$, morphology of the cylindrical microdomains with macroscopically random orientation was re-formed from the block polymers in disordered state. Molecular interpretations of observed morphological changes were presented. Residual deformation in bulk specimens and anomalous behavior of birefringence of the specimens with annealing temperature were interpreted phenomenologically on the basis of a "two-state" model.

I. Introduction

Polystyrene–polybutadiene–polystyrene (SBS) block polymers having a domain structure of alternating lamellar or of cylindrical microdomains of polystyrene (PS) component in the matrix of polybutadiene (PB) behave initially as a plastic material when stretched at temperatures below the glass-transition temperature (T_g) of PS. However, when they are stretched beyond the yield point they become rubbery, with high elasticity and large elastic deformation.[1-5] This is a phenomenon known as "strain-induced plastic-to-rubber transition". It is believed that the yielding process involves fragmentation of the original glassy domains that, even being fragmented, preserve properties of glassy material and play the roles of physical cross-links and fillers for the highly stretched rubbery matrix.[6,7] It was also observed that after the sample was stretched and the external stress removed, the sample recovers to almost its original length, and the structure can heal to the original one by annealing even at temperatures below T_g of PS.[2-4]

There are, however, no systematic researches about structural changes and relaxations induced by heat treatments in the deformed state. It is expected that the stretched samples of SBS block polymers will break up when heated above T_g because above the T_g the polystyrene domains cannot resist stresses exerted by highly stretched polybutadiene parts of molecules. This is probably why the thermally induced morphological changes in oriented block polymers have not been studied so far at temperatures above the glass transition. In order to circumvent this difficulty we used a special method that ensures constant dimensions of samples and does not involve sample breakage during annealing. The test specimens used in this work are SBS block polymers having the morphology of cylindrical PS domains in a matrix of PB in undeformed state. The deformation mechanism of these samples was systematically studied in our previous paper.[6]

Studies on thermally induced morphological changes and relaxations of block polymers, while keeping their bulk dimension constant, may have the following scientific and practical significance. (i) They should lead to molecular understandings of the domain–deformation mechanism and structural and molecular relaxations (i.e., "self-organization"[16]) processes. (ii) They should also provide fundamental information in regard to control of domain orientation. The highly stretched block polymers have the particular morphology and orientation of domains described in detail in our previous work.[6] Questions will

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