Structure and Properties of Water-Soluble *p*-Carboxybenzyl Polysaccharide Derivatives

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ABSTRACT: A series of water-soluble and water-insoluble heteroxylans, citrus pectin, and both starch components, amylose and amylopectin, were hydrophobically modified by introducing low amounts of *p*-carboxybenzyl groups at constant reaction conditions. The achieved degree of substitution ranged from 0.03 to 0.22. The derivatives were characterized by chemical and spectral analyses. They exhibited tensioactive properties evaluated by various surface-activity tests. The results indicate a weak surface tension-lowering effect and low foamability of all derivatives. However, significant emulsifying and protein foam-stabilizing effects were found for most of the studied derivatives, the most pronounced for the modified pectin and acidic xylans. The rheological behavior of the derivatives was investigated by rotational and oscillation rheometry. The results indicated that the hydrophobic interactions lowered significantly the apparent viscosity of the xylan dispersions and introduced changes, particularly in their flow properties. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 1191–1199, 2000

Key words: xylan; pectin; amylose; amylopectin; *p*-carboxybenzyl ether; emulsifying activity; foam stabilization; rheological behavior

INTRODUCTION

Selective enzymic and chemical modifications have facilitated the preparation of polysaccharide derivatives with novel applications.[1] The most important application of soluble polysaccharides are based on their ability to modify the properties of aqueous solutions. The growing demand for natural and biodegradable surfactants has evoked a renewed interest in amphiphilic carbohydrate polymers. Several reports concern amphiphilic derivatives prepared from commercial[2–8] as well as noncommercial polysaccharides.[9–12]

The solubility of many plant polysaccharides in water is rather poor, particularly in the case of low-branched, linear types. Modification of the polysaccharides with charged substituents helps to overcome this problem. As reported in a previous article,[13] the introduction of *p*-carboxybenzyl (CB) groups imparts water solubility to the formerly partially soluble beechwood xylan and its chain degradation could be minimized by appropriate optimum reaction conditions.

To achieve a moderate hydrophobization without loss of water solubility, the CB derivatives of a series of plant polysaccharides (various heteroxylan types, amylose, amylopectin, and pectin) were prepared at the optimum reaction conditions established for glucuronoxylan.[13] In this article, we describe their chemical, molecular, and some functional properties.

EXPERIMENTAL

Materials and Chemicals

The Na⁺ salt of the 4-*O*-methylglucuronoxylan from beechwood (GX) and water-soluble arabinoglucu-

Table I   Sugar Composition of the Polysaccharide Raw Materials

Sample	Structural Type	Sugar Composition (Relative Wt %)				
		Ara	Xyl	Glc	Gal	UA[a]
GX	(4-*O*-Me-Glucurono)xylan	—	81.1	2.0	0.5	16.4
LGX	*wis*-(4-*O*-Me-Glucurono)xylan	—	92.5	3.6	0.2	3.7
AGX	*ws*-Arabino(glucurono)xylan	13.2	74.5	1.0	2.7	8.6
RAX	*wis*-Arabinoxylan	12.0	85.9	2.1	—	tr
CHX	*ws*-Heteroxylan	31.7	48.3	8.0	7.2	4.8
AM	Amylose	—	—	100	—	—
AP	Amylopectin	—	—	100	—	—
P	Polygalacturonate K$^+$	1.6	0.6	1.2	6.6	90

tr, traces.

[a] 4-*O*-Methylglucuronic acid.

ronoxylan (AGX) were prepared in a semitechnical scale from beech wood meal[14] and corn cobs,[15] respectively. The water-insoluble glucuronoxylan isolated from the viscose effluents (GXL) was a gift from Lenzing AG (Lenzing, Austria). The water-insoluble arabinoxylan (RAX) was isolated from rye bran,[16] and the heteroxylan (CHX), from corn hulls.[17] Amylose (AM) and amylopectin (AP) were purchased from Serva (Heidelberg, Germany). The K$^+$ salt of polygalacturonate (P) was prepared from citrus pectin (Fluka, Steinheim, Germany) in our laboratory. Bovine serum albumin (BSA) was from Sigma Chemical Co. (St. Louis, MO). The analytical characteristics of the polysaccharide samples are given in Table I.

Methods

The carboxyl groups of the xylan-type derivatives which comprise those of the glucuronic acid com-

Table II   Yield and DS$_{CB}$ of the *ws*-CB Polysaccharide Derivatives

Sample	Yield (g/g)	DS$_{CB}$		
		(a)	(b)	(c)
GXa	0.92	0.08	0.09	
GXb	0.98	0.11	0.10	
GXL	0.45	0.03		
AGX	0.98	0.16	0.14	
CHX	0.95	0.12		0.15
RAX	0.64	0.22	0.23	
AM	0.71	0.14	0.13	
AP	0.82	0.16		
P	0.89	nd	0.04	0.03

nd, not determined.

(a) Determined by potentiometric titration. (b) Estimated from the ^{13}C-NMR spectra. (c) Derived from the FTIR calibration curve.

ponent and CB substituent were determined by potentiometric titration of the protonated samples, as previously described.[13] The degree of substitution with CB groups (DS$_{CB,X}$) for the xylan derivatives was calculated according to equation
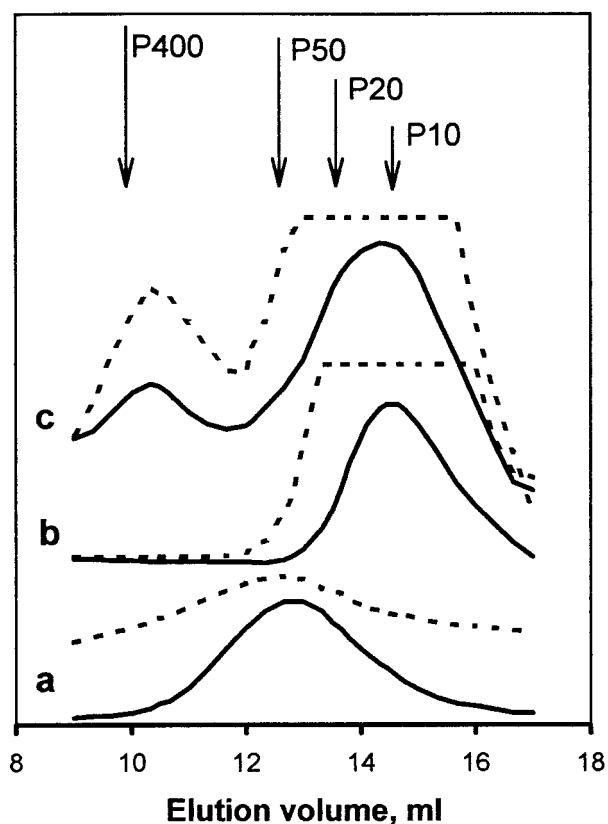

Figure 1   HPGPC chromatograms of the *ws* derivatives (a) CB–P, (b) CB–AP, and (c) CB–GXa recorded by (full line) refractometric and (dotted line) UV$_{254}$ detectors. The arrows indicate the elution volume of the pullulan standards P10, P2O, P50, and P400 used for calibration.

Table III   Molecular Characteristics of the Parent Polysaccharides and Their *ws*-CB Derivatives

| Sample | $[\eta]^a$ (mL/g) | HPGPC on Separon HEMA-BIO 1000 | | |
		$M_w \times 10^{-3}$	M_w/M_n	Area (%)
GXa	63.0	41[b]	1.21	95
CB–GXa	58.9	40[b]	1.43	87
AGX	75.0	68[b]	2.00	92
CB–AGX	70.1	122[b]	2.10	96
RAX	265.2[c]	nd	nd	nd
CB–RAX	131.0	252[b]	1.37	77
CHX	nd	140[e]	1.55	76
CB–CHX	100.2	251	2.34	100
AM	nd	nd	nd	nd
CB–AM	nd	39	1.85	99
AP	nd	nd	nd	nd
CB–AP	6.2	24[e]	1.26	95
P	93.0	123	1.75	100
CB–P	80	113[b]	1.82	94

[a] Measured in $0.1M$ NaNO$_3$.
[b] Presence of a molecular peak at $M_w > 500$ kDa.
[c] Measured in DMSO.
[d] Presence of a molecular peak at $M_w \sim 21$ kDa.
[e] Presence of a molecular peak at $M_w \sim 5$ kDa.

$$\mathrm{DS_{CB,X}} = [Q(0.132 + 0.056\,\mathrm{DS_{UA}})$$
$$\div (1 - 0.135Q)] - \mathrm{DS_{UA}}$$

where Q is the total carboxyl group content in mmol/g, and $\mathrm{DS_{UA}}$, the degree of substitution of the xylan chain by 4-*O*-methyl-D-glucuronic acid units with the molar mass of 191. The molar masses of the xylopyranose unit and the CB group are 132 and 135, respectively. In the case of the glucan-derived CB derivatives, the degree of substitution was calculated according to the equation

$$\mathrm{DS_{CB,G}} = 162Q/(1000 - 135Q)$$

where 162 is the molar mass of the glucopyranose unit.

FTIR spectra were measured in KBr pellets (2 mg sample/200 mg KBr) using a Nicolet Magna 750 spectrophotometer operating at 4 cm^{-1} resolution. ^{13}C-NMR spectra (75.4 MHz) were recorded with an FT-NMR spectrometer (Bruker Avance DPXM 300) at 40°C equipped with a selective excitation unit and gradient-enhanced spectroscopy kit (GRASP) for generation of Z gradients up to 50 Gauss/cm in a 5-mm inverse probe. For the identification of CH$_2$ groups, the DEPT sequence was used from the standard Bruker software library.

Solution viscosity was measured in $0.1M$ NaCl at 20 ± 0.1°C using an Ubbelohde cappilary viscometer. High-pressure gel permeation chromatography (HPGPC) was performed on Separon HEMA-BIO S1000 columns, calibrated with pullulan standards, as previously described.[13] All samples were measured at the same polymer concentration (3 mg/mL) in $0.1M$ NaNO$_3$ and the elution was recorded by refractometry (RI) and UV absorption at 254 nm (UV$_{254}$). Rheological measurements were performed in distilled water at 20 ± 0.1°C on a Rheotest 2 (2–50 Hz; VEB MLW, Medingen, GDR) over the shear rate range of 1.5–1312 s^{-1} and at 30 ± 0.1°C on a Rheometrics RECAP II (USA, frequency sweep; oscillation frequencies ranged from 10^{-1} to 10^2 rad s^{-1}). The polysaccharide dispersions were prepared by pre-swelling the samples in water for 1 h at ambient temperature and subsequent thorough stirring for 1 h. Then, the dispersions were left to stand at 10°C overnight. For the rotational experiments, the shear rate was changed stepwise and the samples were sheared until a constant shear stress was reached. The interfacial properties, including surface tension ($\gamma_{\min}$), critical micelle con-

centration (c.m.c.), foamability, emulsifying efficiency, and protein (BSA) foam-stabilizing activity, were characterized by methods described in detail in a previous article.[12]

Preparation of CB Polysaccharide Derivatives

The CB derivatives of the polysaccharide samples were prepared by reaction with *p*-carboxybenzyl bromide of the polysaccharides in aqueous alkali at ambient temperature for 24 h.[13] Each derivative was isolated from the reaction medium by precipitation with four volumes of ethanol and the precipitated product was separated by centrifugation. After repeated washing with 80% ethanol, the product was redispersed in distilled water, stirred for 4 h, and subjected to dialysis. The nondialyzable, soluble (*ws*) portion was separated by centrifugation from the insoluble (*wis*) part and both portions were lyophilized.

RESULTS AND DISCUSSION

Structural and Molecular Properties

A series of CB derivatives was prepared from various heteroxylans, α-glucans, and citrus polygalacturonate (K^+ salt) by reaction with *p*-carboxybenzyl bromide in aqueous alkali at ambient temperature.[13] The yields of the *ws* preparations varied between 0.45 and 0.98 g/g polysaccharide (Table II). The CB substituent reveals a strong UV absorption maximum at 240 nm.[13] In Figure 1, the HPGPC records of CB–GXa, CB–AP, and CB–P are displayed as examples. For all derivatives, the chromatograms obtained by RI as well as UV detection at 254 nm showed the same pattern, which indicates the distribution of CB groups over all macromolecular chains. The intrinsic viscosities [η] and apparent molecular masses (M_w) derived from the HPGPC experiments are summarized in Table III.

The presence of CB groups was indicated also by IR spectroscopy. As seen in Figure 2, the FTIR spectra of all *ws*- and *wis*-CB derivatives exhibit absorption bands at ~1551 and 777 cm^{-1} attributed to $\nu_{as}(COO^-)$ and benzene-ring vibrations, respectively, typical of the CB substituent.[13] The DS_{CB} was calculated based on the carboxyl group content of the CB derivative and taking into account the uronic acid content of the parent polysaccharide (see Experimental). The obtained data are summarized in Table II. The ^{13}C-NMR spectra of the derivatives, displayed for CB–GX, CB–
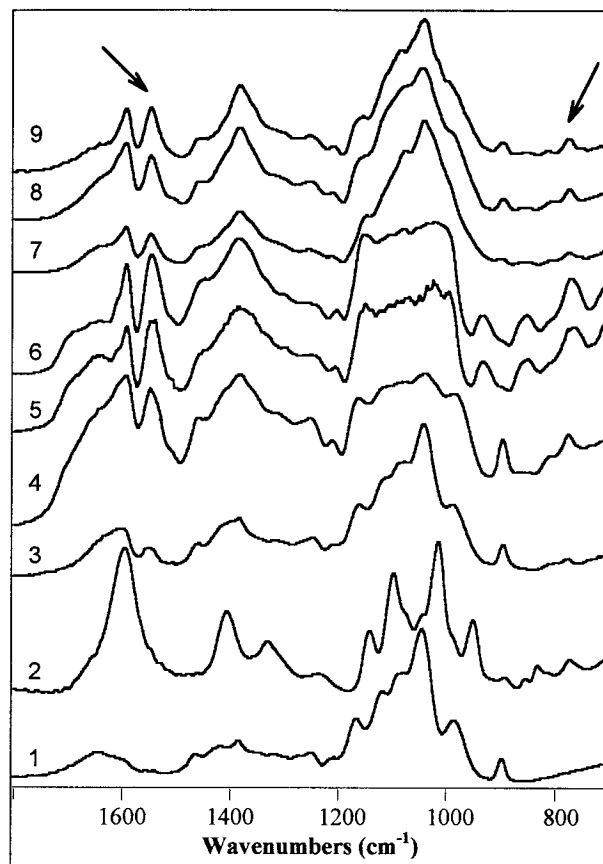

Figure 2 FTIR spectra of the CB derivatives of (1) *ws*-GXL, (2) P, (3) *wis*-GXa, (4) *ws*-GXa, (5) *ws*-AP, (6) *ws*-AM, (7) CHX, (8) AGX, and (9) *ws*-RAX.

AM, and CB–P in Figure 3, showed signals of the CB substituent[18] at δ 142.1–142.5 (Ca), 129.3–129.6 (Cb,f), 130.1–130.4 (Cc,e), 136.6–137.0 (Cd), and 74.3–75.5 (CH$_2$). The carboxybenzylation of the hydroxyl groups was not selective. Substitution took place at both secondary OH groups of the xylose residues, indicated by the appearance of substituted C-2 and C-3 carbon signals at δ 82–83 ppm and at all possible sites of the glucan chains documented by new signals at δ 80–82 and 66 due to substitution at positions O-2, O-3, and O-6, respectively.[19,20]

The DS_{CB} of some of the *ws*-CB derivatives were roughly estimated by comparing the integrated areas of the resonances for the aromatic carbons (δ 129–130) and the known anomeric carbon chemical shifts of the studied polysaccharides which ranged between δ 97 and 110.[19–21] The obtained values, included in Table II, accorded well with those calculated from the potentiometric analyses. By plotting the later DS_{CB} values against the peak absorbance ratios A_{1551}/A_{1450}, a
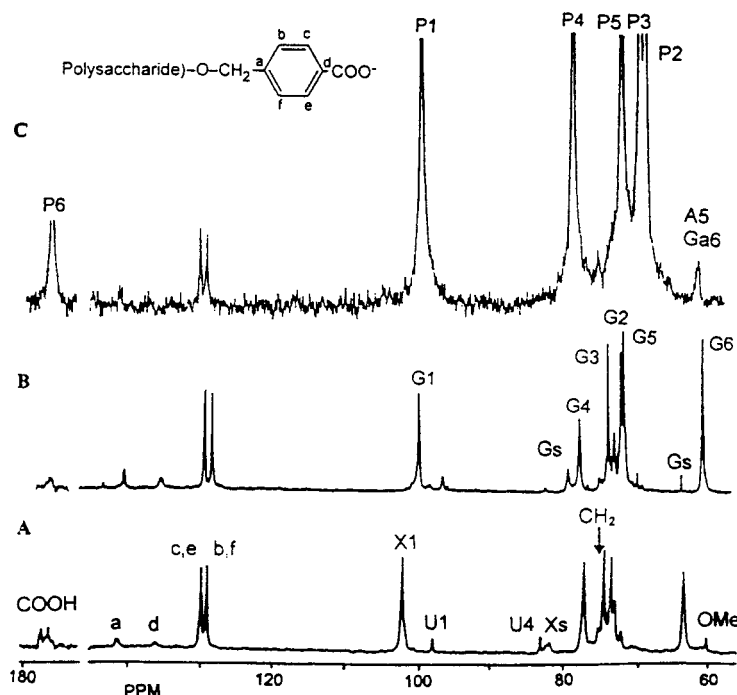
Figure 3 ^{13}C-NMR spectra (in D_2O) of (A) CB–GXa, (B) CB–AM, and (C) CB–P. X, β-D-Xyl*p*; U, 4-*O*-Me-α-D-GlcA*p*; G, α-D-Glc*p*; P, α-D-GalA*p*; Ga, β-D-Gal*p*; A, α-L-Ara*f*; s, substituted carbon.

valid linear relationship was obtained (Fig. 4). It can be used as a calibration curve to estimate the DS_{CB} of CB polysaccharide derivatives by the
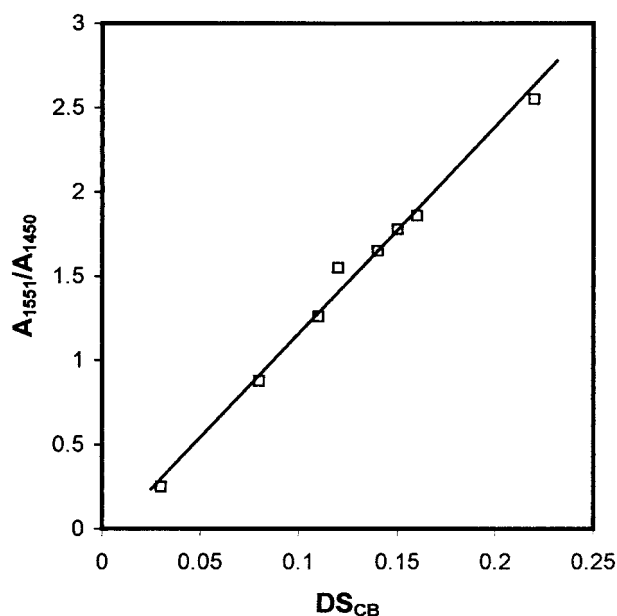

Figure 4   Correlation between DSCB, determined by potentiometric titration of the CB–polysaccharide derivatives and the absorbance ratio $A_{1551cm^{-1}}/A_{1450cm^{-1}}$ (peak/valley).

rapid FTIR technique. In this way, the low DS_{CB} of CB–P could be estimated and was in accord with the NMR-derived value, whereas the potentiometric method gave no reproducible value. On the other hand, the low DS_{CB} (0.03) of CB–GXL potentiometrically determined fitted well in the calibration curve. In the case of CB–CHX, the calculated DS_{CB} value is underestimated, probably due to the high proportion of glucose in the sample which was not taken into account using eq. (1).

In spite of the constant reaction conditions used, the DS_{CB} of the *ws* derivatives ranged between 0.03 and 0.22. Together with the yields, these results reflect the different reactivity of the polysaccharides affected by solubility. As expected, the least reactive were the originally water-insoluble samples for which the alkylation reaction proceeded under very heterogeneous reaction conditions, giving lower yields and relatively higher DS_{CB} values of the *ws* portion. The water-soluble xylans as well as pectate gave rather high yields of the CB derivative, but lower DS_{CB}, particularly the last mentioned. Also, note that the *wis* portions of the CB derivatives contained low amounts of CB groups as seen by IR spectroscopy; however, the amount was not sufficient enough to solubilize the molecules.

Table IV   Surface Tension (γ_{min}), Foamability, and Emulsification Efficiency of the *ws*-CB Derivatives of Polysaccharides

Sample	γ_{min} (mN m^{-1})	Foamability (%)	Oil/Cream Layer (mm/mm)		
			h_1	h_2	h_3
GXa	61.0	32	0/1	0/5	0/7
GXb	51.0	40	0/0	0/6	0/6
LGX	66.5	8	1/1	2/2	2/3
AGX	68.8	16	0/0	0/4	0/8
RAX	62.0	32	0/1	0/1	0/8
CHX	71.1	11	0/0.2	0/3	0/8
AM	63.1	16	0/2	2/3	2/4
AP	68.3	8	0/0.4	0/5	0/6
P	49.3	8	0/25	0/17	0/12
D 100 Protein[11]	nd	300	nd	nd	nd
Gum arabic[11]	nd	80	nd	nd	nd
Tween 20	nd	nd	0/0	0/0	0/2

Surface tension was measured at polymer concentration $c = 5$ g L^{-1}. Foam height was related to the height of the original liquid. Emulsification efficiency is the height of the cream layer formed after storage at (h_1) 5 min, (h_2) 30 min, and (h_3) 24 h; all emulsions are of the oil/water type.

Tensioactive Properties

Attachment of CB substitutents imparted, besides solubility, hydrophobic properties to the polysaccharides (Table IV). The effect on the surface tension of water (γ_{min}) was only moderate and most of the dispersions showed no formation of a distinct c.m.c., typical of surfactants. Only the CB derivatives of the acidic xylan GXb and P with a γ_{min} of 51.0 and 49.3 mN m^{-1}, respectively, gave a c.m.c. of 1.25 g L^{-1}. The foamability of all CB derivatives was low in comparison to that of the whipping protein control and even lower than that of the food additive, gum arabic,[11] which is supposed to be a protein–polysaccharide complex.

The xylan-type derivatives, except the low-substituted CB–GXL, exhibited significant emulsifying properties. They formed emulsions of the oil/water type with stabilities comparable to that of the commercial emulgator Tween 20 (oxyethylated monolauransorbitol). The CB derivatives of amylose and amylopectin showed differences in their emulsifying activity. In contrast to CB–AP, an oil layer separated very soon from the emulsion of CB–AM. In spite of the very low DS_{CB}, the modified pectate showed a very high emulsifying efficiency. The cream layer formed was stable even after 5 days of rest without separation of the oil. The stabilizing effect of the CB derivatives on the foam generated by the protein BSA is illustrated in Figure 5. A high foam volume was generated by the control solution of BSA, which di-

minished after heating. The tested derivatives, similarly as the polysaccharide controls, xanthan (Xan) and gum arabic (GA), depressed the evaluation of the BSA foam due to the increased viscosity of the liquid medium. During heating, the presence of polysaccharides appeared to protect gas cells against thermal disruption. As seen, the stabilizing effect of the CB derivatives was high and comparable to that of xanthan for all tested CB derivatives, except of CB–GXL. Otherwise, gum arabic was not able to stabilize the protein foam. By comparing the low-viscosity, high-substituted CB–AP and the high-viscosity, low-substituted CB–P, it was shown that the stabilizing effects were very similar. It seems that more factors, not only viscosity and the degree of hydrophobicity, determine the surface-active properties of polysaccharide-based surfactants.

Rheological Properties

Because hydrophobic moieties can act as crosslinks of a physical network, the rheological properties of the polysaccharides and their CB derivatives were investigated. The intrinsic viscosities of the CB derivatives of all xylans as well as pectin are slightly lower than for the corresponding parent polysaccharides (Table III). This results can be explained by intramolecular associations due to hydrophobic interactions of the polymer chains in a dilute solution[22] and, consequently, in coil contraction or a molecular weight
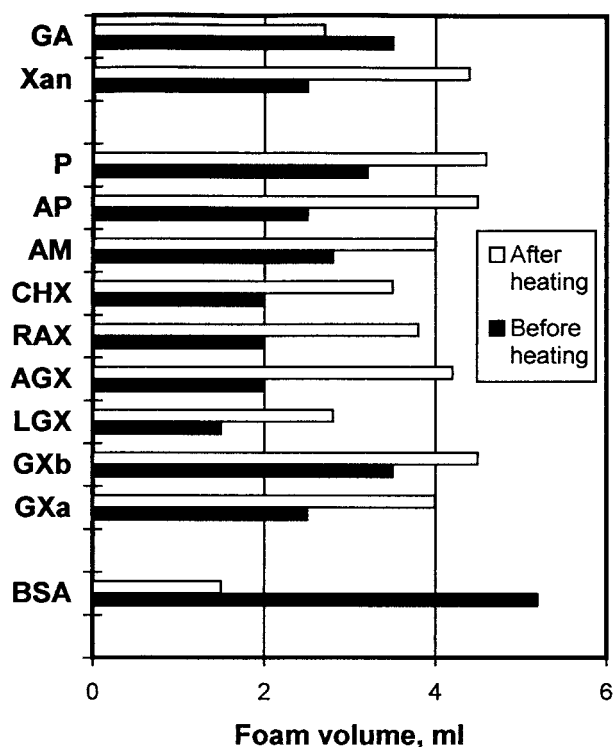
Figure 5 Effect of the CB polysaccharides and controls (xanthan, Xan; gum arabic, GA) on the foam volume of BSA before and after heating at 90°C for 3 min.

degradation. However, sedimentation equilibrium measurements[23] of GX and AGX before and after modification gave very similar molecular weights, that is, ~16,000 for the GX and CB–GX and 37,000/40,000 for AGX and CB–AGX, indicating no significant degradation for these xylans. Therefore, hydrophobic interactions seem to be responsible for the viscosity decrease. According to the report on hydrophobically modified carboxymethylcellulose derivatives,[24] such coil contractions occur at low contents of incorporated aliphatic chains, whereas, at higher contents of alkyl substituents, associative intermolecular interactions were observed in the semidilute range of concentrations affecting the flow properties.

To study changes in the rheological behavior of the structurally different polysaccharides by the CB modification, the flow and viscoelastic properties were examined at an equal polymer concentration of 6.5% (w/w) in distilled water, suggesting that changes can be seen in the semidilute range in all cases. The shear dependencies of the parent and modified couples of GX, AGX, CHX, and P are illustrated in Figure 6. In the low shear range ($D < 100$ s^{-1}), the flow curves (log η_{app} plotted against log D, D being the shear rate) of

all samples exhibit a reduction in the η_{app} with increasing D, which is typical of polymer solutions with shear-thinning or pseudoplastic behavior. The shear dependence of η_{app} is the most pronounced for the parent xylan GX, and its viscosities are over an order higher than for the other polymers studied. Also, GX is only partially water-soluble and the dispersion contains highly swollen particles, supporting the formation of a strong structural network at rest which breaks down by shearing.[25] After CB modification, all xylan samples exhibited lower viscosities in the low shear range, probably due to the predominance of intrachain associations affected by hydrophobic interactions of the CB substituents.[22]

Differences between the xylan samples are evident at higher shear rates ($D > 100$ s^{-1}). The η_{app} of the neutral, highly branched xylan (CHX) lost its shear dependence after modification and the flow curve adopted a Newtonian-like behavior. Conversly, the shear dependence for AGX,
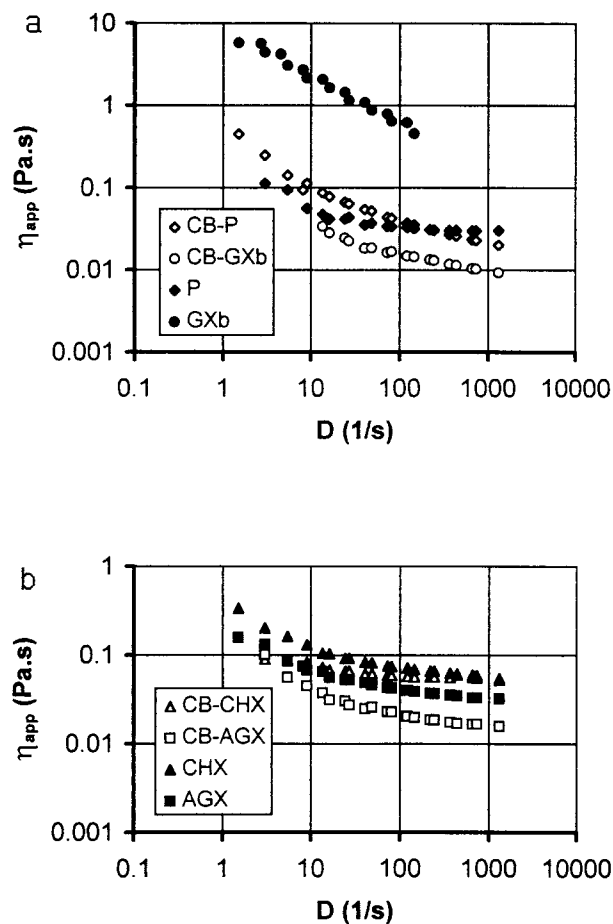

Figure 6 Flow curves at 20°C of the aqueous dispersions (6.5% w/w in distilled water) of the (full symbols) original and (empty symbols) CB-modified polysaccharides.
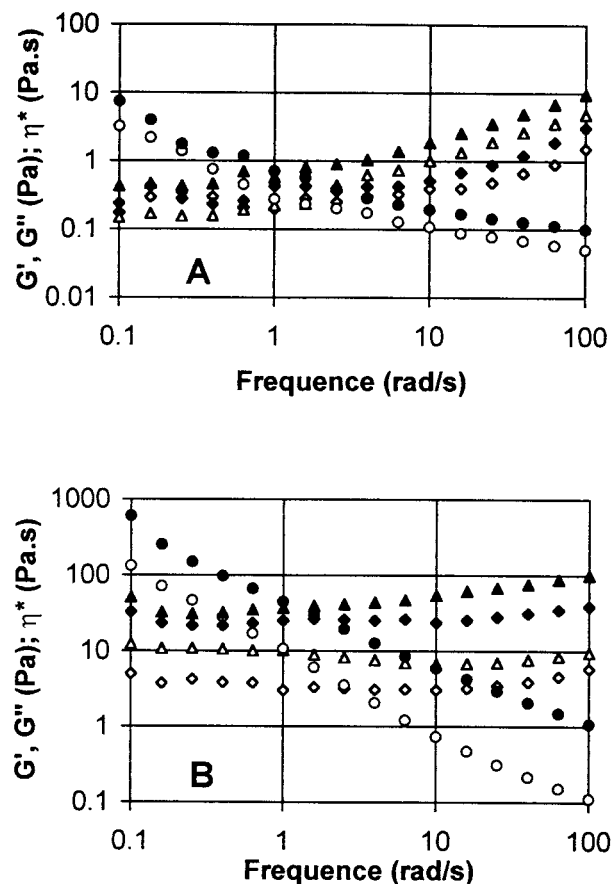
Figure 7 Mechanical spectra of the dispersions (6.5% w/w in distilled water) at 30°C for the (full symbols) original and (empty symbols) CB-modified polysaccharides: (A) CHX and CB–CHX; (B) GXb and CB–GXb; (○) η^*; (△) G'', (◇) G'.

the higher DS_{CB} of this xylan (Table III) as well. In the case of CB–GX, the η_{app} decreased without a substantial change of the shear dependence. After introduction of a very small amount of CB substitutents to the polygalacturonate, the derivative (CB–P) became strongly shear-dependent in the whole shear range.

The mechanical spectra of the parent and CB-modified polysaccharides, shown for GXb and CHX in Figure 7, are typical of liquidlike dispersions with $G'' > G'$ in the whole frequency range and tan δ > 1 (Table V). Both moduli (G'' and G') of CHX and CB–CHX are strongly frequency-dependent, in contrast to those of GXb and CB–GXb. This can be explained by the existence of network formation in the last mentioned couple, which resists the oscillation. Note that at higher polymer concentrations (>7%) the GX dispersions exhibit "weak gel"-to-gel-like properties.[26] The slight increase of tan δ for CB–GXb indicates that the xylan became more liquidlike after modification, which is in accord with the described flow-property changes. At equivalent numerical values of shear rate (s^{-1}) and frequency (rad s^{-1}), the corresponding η_{app} were lower than was the complex viscosity η^*. Such departure from the Cox–Merz rule[27] is a characteristic feature of networks which can survive low amplitude oscillatory deformation but are broken down under shear.

CONCLUSIONS

The functional properties, including tensioactive effects and rheological behavior, of the CB polysaccharide are significantly structure-dependent. The hydrophobization effect of the CB substitution was particularly high in the case of acidic polysaccha-

containing a small amount of uronic acid side chains, increased after modification. This indicates a stronger contribution to network formation by the substituents, but may be affected by

Table V   Rheological Data of the Original and *ws*-CB Polysaccharide Derivatives

| Sample | η_{app} (Pa s) | | G' (Pa) | G'' (Pa) | | η^* (Pa s) | |
	$D = 9\ s^{-1}$	$D = 121\ s^{-1}$	1 Hz	1 Hz	tan δ	1 Hz	10 Hz
GXb	0.635	0.131	26.3	47.0	1.79	1.49	1.79
CB–GXb	0.037	0.013	3.12	6.95	2.23	1.21	0.15
AGX	0.052	0.028	0.50	1.70	3.39	0.28	0.07
CB–AGX	0.030	0.015	0.34	0.44	1.29	0.09	0.01
CHX	0.105	0.050	0.43	1.38	3.23	0.23	0.11
CB–CHX	0.067	0.040	0.30	0.74	2.43	0.13	0.06
P	0.045	0.025	nd	nd	nd	nd	nd
CB–P	0.079	0.028	0.62	1.58	2.54	0.27	0.10

Polymer concentration: 6.5%; temperature: 30°C.

rides such as pectate and glucuronoxylan, probably due to a proper hydrophilic/hydrophobic balance.

An advantage of the described CB modification is that the polysaccharide chains are labeled with an UV-absorbing substitutent. Suggesting a high conversion of the derivatives and nonsignificant degradation, the CB-modification could be utilized in analytical procedures such as in the determination of the molecular mass by the UV-scanning analytical ultracentrifuge[23] or in interaction studies.

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