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Solution interactions and rheology of *N*-[2-(glycosyloxy)ethyl]chitosan derivatives*

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ABSTRACT

Aqueous solutions of *N*-[2-(glycosyloxy)ethyl]chitosans have been studied by steady-shear rheometry over an intermediate shear-rate range (1–2500 s^{-1}). The power law has been found to be a suitable model for characterizing the rheological behavior of these solutions over the shear-rate range examined. In general, solution viscosity and pseudoplasticity increased as the degree of substitution (d.s.) decreased. This trend also applied to measurements of intrinsic viscosity. The solutions of derivatives having pendant lactose residues were less viscous than those having equivalent pendant monosaccharide substitution. It was also found that derivatives bearing neutral monosaccharide branches interacted with xanthan polymer in solution.

INTRODUCTION

Interest in branched polysaccharides arises in part from some of their useful physical properties in water solution[1-3]. Similarly, motivation for modifying polysaccharides stems in part from a desire to impart or control solution properties[4]. Some methods for preparing branched polysaccharide derivatives have been reported[4-7], and discussed with regard to their advantages and disadvantages[4].

In the case of natural branched polysaccharides, the relatively limited array of structurally related materials makes it difficult to establish a predictive understanding of structure–property trends. Conversely, most chemically modified derivatives are often too complex to establish any correlation between their structure and function. A better understanding of such an interrelationship is desirable, and would ultimately lead to the ability to tailor solution properties by structural variation of the polymer molecules.

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* Part II of the series *N*-[2-(glycosyloxy)ethyl]chitosan derivatives: For part I, see ref. 9.

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We have reported the preparation of an array of chitosan derivatives having *N*-(2-glycosyloxyethyl) branches on the 2-amino position[8,9]. While these compounds are not branched glycosidically, they do contain intact glycoside residues attached via a C_2 spacer unit. This methodology allowed us to vary the saccharide identity and thereby provide a family of derivatives having monosaccharide branches with various functionalities, both α and β glycosidic configurations, as well as disaccharide substituents. All of these derivatives were obtained with degrees of substitution (d.s.) over the range from 0.25 to 1.0.

RESULTS AND DISCUSSION

Steady-shear rheometry was performed on 2.0% (w/w) solutions (unless otherwise specified) of polysaccharide derivatives and commercially available polysaccharides, in distilled water at 20 ± 0.5°. Measurements were performed with a controlled stress rotational viscometer having cone and plate geometry, from which shear stress (σ) values at shear rates ($\dot{\gamma}$) ranging from 1–2500 s^{-1}, were obtained. Apparent viscosities (η) were determined according to Eq. *1*:

$$\eta = \frac{\sigma}{\dot{\gamma}} \qquad (1)$$

The shear-rate dependence of the polymer solution viscosities could be modelled using the power law[10,11]:

$$\sigma = m\dot{\gamma}^{n} \qquad (2a)$$
$$\eta = m\dot{\gamma}^{(n-1)} \qquad (2b)$$

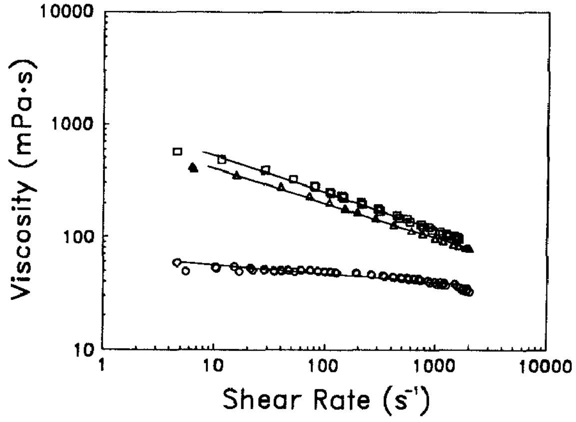


Fig. 1. Rheograms of apparent viscosity *vs.* shear rate for derivatives **6a** (○), **6b** (△), and **6c** (□) on logarithmic coordinates.

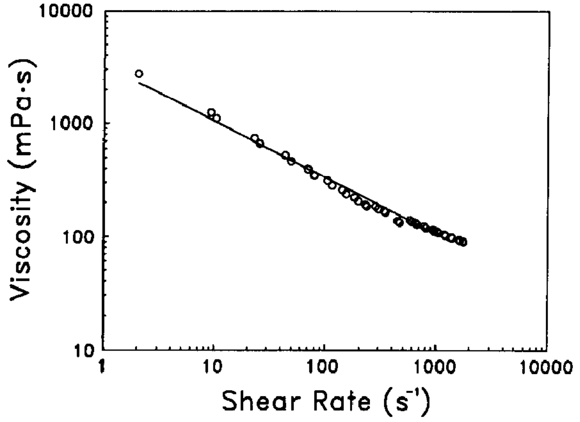


Fig. 2. Rheograms of apparent viscosity *vs.* shear rate for derivative **6d** (○), on logarithmic coordinates.

TABLE I

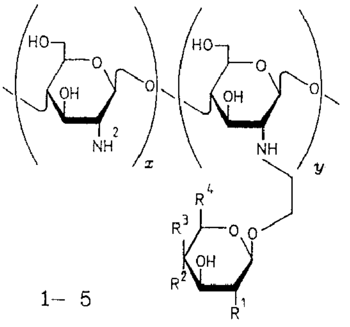
Power-law parameters for branched chitosan derivative solutions (2.0 % w/w in water), xanthan gum (Xan), *O*-(hydroxyethyl)cellulose (HEC), and sodium alginate (NaALG)

Derivative	*Branch*	*d.s.* (±*0.05*)	*n*	*m* (*mPa·s*)	r^2	*No. of points*
1a	β-Glc	1.00	1.01	22.4	0.998	8
2a	β-Gal	1.00	0.879	82.7	0.999	36
2b		0.70	0.783	434	0.997	33
2c		0.38	0.588	2300	0.995	50
3a	β-GlcA	1.00	0.970	45	0.999	36
3b		0.67	0.911	109	0.997	32
4a	β-Lact	0.90	0.997	24.9	0.999	53
4b		0.76	0.939	49.4	0.999	28
4c		0.35	0.841	222	0.997	30
4d		0.32	0.891	159	0.997	34
4e		0.24	(gel)			
5a	β-GlcNAc	1.00	1.05	14.3	0.999	24
6a	α-Glc	1.00	0.929	65.1	0.998	62
6b		0.59	0.695	803	0.999	34
6c		0.38	0.677	1090	0.998	33
6d[a]		0.26	0.502	3270	0.988	41
7a	α-Gal	1.00	1.00	25.3	0.999	56
7b		0.86	0.931	54.1	0.999	59
7c		0.48	0.554	5180	0.992	43
7d		0.32	0.778	525	0.998	60
8a	α-GlcNAc	1.00	(gel)			
8b		1.00	(gel)			
8c		0.35	0.864	196	0.997	29
8d		0.19	0.822	456	0.994	31
8e		0.17	0.810	456	0.996	36
9	α-GlcNH$_2$	1.00	0.845	110	0.999	37
2.0 % Xan			0.296	10200	0.938	38
2.0 % HEC			0.426	9230	0.985	24
2.0 % NaALG			0.717	3180	0.988	34

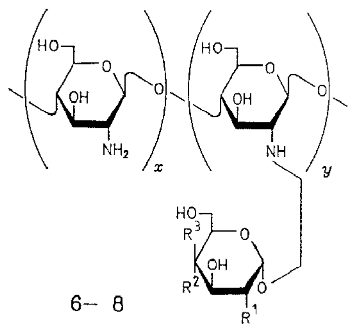
[a] Data given is for a 1.0 % solution.

where *n* is the flow behavior index, and *m* is the consistency coefficient. Some typical rheograms for the polymer solutions are shown in Figs. 1 and 2 as η *vs.* $\dot{\gamma}$ on logarithmic coordinates. Table I gives the power-law parameters *m* and *n* for all of the solutions as well as the coefficient of determination (r^2) for each rheogram. The linear nature of the rheograms (Fig. 1) and high r^2 values indicate that the power-law model accurately describes the polymer solution flow properties over the range of conditions studied. This representation of flow behavior was felt to be superior to examination of apparent viscosities at zero-shear viscosity (η_0) or at specific shear-rate values within the experimental range (for example 10 and 1000 s^{-1}). The flow behavior index is an indication of shear-rate thinning (pseudoplasticity) or non-Newtonian nature of the solution, while the consistency coefficient is numerically equivalent to the viscosity at $\dot{\gamma} = 1\ s^{-1}$. In contrast to Newtonian fluids which have flow indices of 1, shear thinning solutions of high-molecular-weight polysaccharides will have *n*-values less than one.

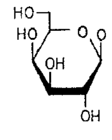
The first notable trend in the rheological properties of the derivative solutions was that the fully substituted derivatives **1a–3a** and **5a–7a** and the highly substituted lactosyl compound **4a** showed Newtonian flow behavior, or nearly so, as indicated by power-law indices close to 1.0. This may be indicative of relatively little polymer interchain interaction at low-shear conditions, and little change in polymer association at higher shear rates. Derivatives **2a** and **6a** were slightly anomalous in that they had *n* values of ~ 0.9, and thus a small shear-rate dependence. A possible explanation is that these derivatives are capable of stronger self-association than the other highly substituted derivatives. However, despite these minor variations it is obvious that all solutions of



1– 5



6– 8

	R^1	R^2	R^3	R^4
1, 6	OH	OH	H	CH_2OH
2, 7	OH	H	OH	CH_2OH
3	OH	OH	H	CO_2H
4, 8	NHAc	OH	H	CH_2OH
5	OH		H	CH_2OH

highly substituted derivatives exhibit low shear-rate dependence. The consistency coefficient or *m* parameter for the high d.s. derivatives ranged from 14–80 mPa·s^n, compared to water with a viscosity of 1.0 mPa·s at the same temperature.

A related observation was the increase in *m* and decrease in *n* as the d.s. decreased for derivatives containing the same branch. For example, of the β-galactosyl series **2a–c** solutions of polymer, **2c** with a d.s. of 0.38, was considerably more viscous (m = 2300 mPa·s^n) and pseudoplastic (n = 0.588) than **2b** (m = 434 mPa·s^n and n = 0.783). A similar trend was seen in the α-D-glucosyl, β-D-lactosyl, 2-acetamido-2-deoxy-α-D-glucosyl and β-D-galactosyl series. In the lactosyl series, **4a–d**, the magnitude of the change was considerably less, both in terms of viscosity and pseudoplasticity. This was undoubtedly a result of the larger substituent being able to have interchain interactions only at low levels of substitution. All of these observations indicated that samples of low d.s. were more capable of interchain associations. Two possible mechanisms for this are: (1) interdigitation of chains, and (2) occurrence of interchain interactions analogous to those present in native chitosan[12]. For the latter case, a particular conformational state might provide "open" and "branched" faces, much like those proposed in seed galactomannan self-associations[3,13,14]. The "open" faces could then interact, much as does native chitosan, with regions of disruption imparting overall solubility. The latter model may provide an explanation for the apparently anomalous result for derivative **7c**, which had a d.s. of 0.48 and was considerably more viscous than the analogous derivative **7d**, which had d.s. = 0.32. Assuming that interactions do occur as proposed, it is reasonable that an optimum degree of substitution and substitution pattern will exist for maximum interchain association. Indeed, recent studies have shown that both substitution pattern and degree of branching greatly influenced galactomannan interactions[13,14]. Thus, perhaps for this system a random substitution of ~ 50% is near optimum and viscous properties decrease on either side of this value. Of course, it is likely that viscosity and pseudoplasticity would increase again at quite low d.s. values, as larger blocks of unsubstituted backbone adopt chitosan-like interactions, eventually resulting in gels and insolubilization. Derivatives **4e** and **6d**, having d.s. <0.3 and giving a gel and a very viscous solution, respectively, provide some support for this proposal. Fig. 3 shows the experimental data plotted as *n vs* d.s., for neutral monosaccharide branched derivatives, and the dotted line represents the relationship already proposed. Also, it should be expected that derivatives of the type prepared here would have behavior most similar to that of natural branched polysaccharides bearing single pendant residues, such as the galactomannans[13-15].

It must be remembered that 2.0% (w/w) solutions were used for all derivatives throughout these studies; thus, the molar concentration of the solutions varied with the degree of substitution of the sample. It may be reasoned that a fully substituted derivative at 2.0% concentration will have fewer polymer chains (67%) than a derivatives having d.s. of 0.5. However, it is considered that these concentration discrepancies could not account for the changes in solution rheology that were observed. Tests performed on a 2.7% solution of the lactosyl derivative **4a** having d.s. 0.9, showed that it did not vary substantially in rheology from its 2.0% solution, and did not match the 2.0% solution of **4b** having a molar concentration ~ 20% lower.

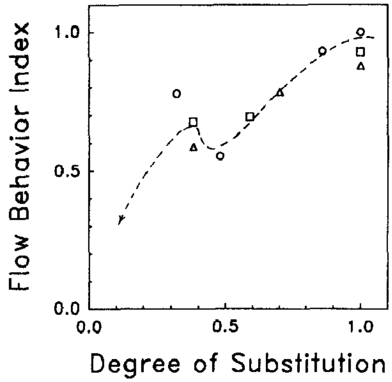


Fig. 3. Plot of the flow behavior index (n) against degree of substitution (d.s.) for derivatives bearing monosaccharide branches **2a–c** (△), **6a–c** (□), and **7a–d** (○). Dotted line represents a postulated relationship between n and d.s.

In order to investigate the role of functional groups in the interactions of the branched chitosan derivatives described here, polymers bearing pendant 2-acetamido-2-deoxy-α- and -β-D-glucose and β-D-glucuronate residues were prepared. The solution properties of **8c–e** having 2-acetamido-2-deoxy-α-D-glucose branches, were somewhat anomalous from the rest of the monosaccharide branched compounds. Even at low d.s. values (0.19 and 0.17, respectively for **8d** and **8e**), the solutions were not very pseudoplastic. As reported[9], the coupling efficiencies in the preparation of these compounds were poor, yielding low-d.s. products at relatively high reactant molar rotions, probably because of steric or electrostatic forces. This may also account for the low pseudoplasticity, since as described for the lactosyl derivatives, a bulkier substituent would probably interfere in the interchain association. The derivative **5a**, which contained the 2-acetamido-2-deoxy-β-D-glucose moiety also seems to fit this trend. However, if the sugar size influenced both the reaction efficiency and resultant solution properties, it seems somewhat surprising that, at a mol ratio of 3.0, fully substituted derivatives **5a**, **8a**, and **8b** were readily obtained. Another interesting result was obtained for **8a** in the 2-acetamido-2-deoxy-glucose series. Surprisingly, this fully substituted derivative did not dissolve in water or aqueous acetic acid, but formed a clear rigid gel. This behavior was anomalous when compared to **5a**, the fully substituted β-analogue, which was soluble in water. As reported elsewhere[9], the ^{13}C-n.m.r. spectrum showed that **8a** actually contained both 2-acetamido-2-deoxy-α- and β-D-glucose residues in 7:1 ratio. When derivative **8b**, having only 2-acetamido-2-deoxy-α- and β-D-glucose branches was prepared, it was also found to be soluble in water. Thus, in contrast to **8b** and **5a** containing pure 2-acetamido-2-deoxy-α- and -β-D-glucose substituents respectively, **8a** gave a gel, seemingly because of the combined presence of both the α and β anomers as co-branches.

The *N*-deacetylation of **8b** having 2-acetamido-2-deoxy-α-glucose branches with d.s. 1.0, was undertaken in order to provide the free amino derivative **9**. It is somewhat inappropriate to compare directly the solution properties of **9** to the other derivatives because of the extra chemical, and potentially degradative treatment required for its preparation[9]. However, as degradation would result in a lower solution viscosity, and as **9** actually showed an increased viscosity compared with **5a** the result implies that free amines take part in some sort of stronger interchain interactions. If any depolymerization did occur, it was masked by the increased viscosity caused by self-association.

Derivatives **3a** and **3b**, which contained pendant β-D-glucuronate residues, had some interesting characteristics. The acidic forms of these derivatives were water-insoluble, whereas the sodium salts were readily soluble and gave solutions having relatively low viscosity and little pseudoplastic character. It was hoped that derivatives bearing pendant uronic acid residues might be useful as metal chelates[3,15]. It was found with **3a** and **3b** that the addition of varying amounts of Ca^{2+} and Cu^{2+} ions had no apparent effect on solution properties.

Solutions of commercial samples of xanthan, *O*-(2-hydroxyethyl)cellulose (HEC), and sodium alginate were evaluated, and their power-law parameters determined as in Table I. Among these products, the chitosan derivatives are more similar in rheological properties to HEC, and had similar viscous and pseudoplastic character over the shear-rate range examined. Xanthan is markedly more pseudoplastic, and sodium alginate is less so. Direct contrasts of 2.0 % solutions of **2c** and **7c** with xanthan and sodium alginate, and 1.0 % solutions of **6d**, with xanthan and sodium alginate are displayed in Figs. 4 and 5, respectively. The three polymers, HEC (1.0 %), **6d**, and xanthan show increasing pseudoplasticity, respectively.

Intrinsic viscosities for derivatives **1a**, **3a**, **6a**, **7a**, **7b**, and **7d** were determined in order to further probe the behavior of these derivatives in solution, and the results are presented in Table II. Looking at the intrinsic viscosities for **7a**,**b** and **c**, there is again an increasing trend with decreasing d.s. This trend suggests a relationship between conformation and d.s. that is consistent with the proposed mechanism for self-association. In other words, there is an apparent conformationally related change in the polysaccharide derivatives at lower d.s. values. It then becomes possible, at certain d.s. values, for a

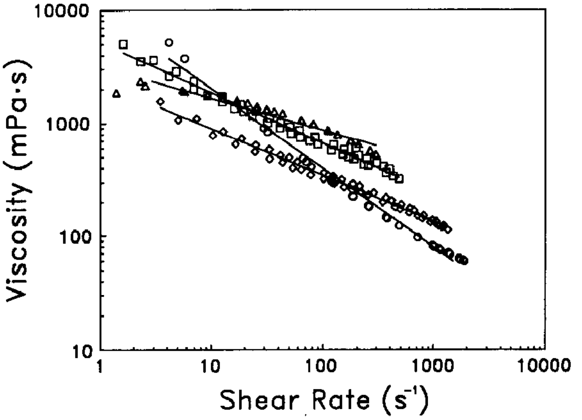


Fig. 4. Rheograms of apparent viscosity *vs.* shear rate contrasting 2.0 % xanthan (○), 2.0 % sodium alginate (△), **2c** (□), and **7c** (□).

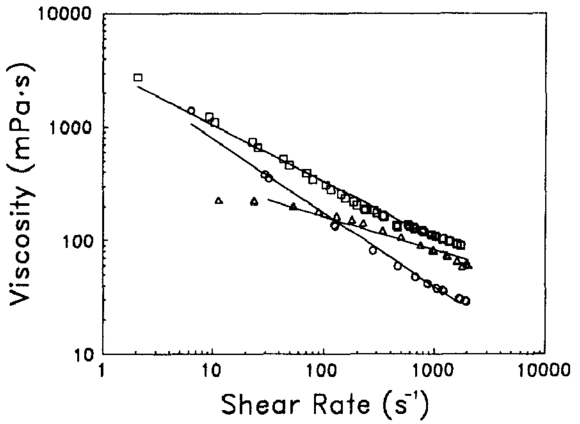


Fig. 5. Rheograms of apparent viscosity *vs.* shear rate contrasting 1.0 % xanthan (○) and 1.0 % sodium alginate (△) with 1.0 % **6d** (□).

maximal inter-chain association to occur, causing increased viscosity and pseudoplasticity. The intrinsic viscosities of the fully substituted derivatives **1a** and **6a**, bearing α- and β-glucosyl groups respectively, are ~ 0.5 and 1.5 (dL/g). This discrepancy could be an indication of greater molecular order in the case of **6a**. The fact that **6a** had lower n (0.929) and m values (65.1 mPa·s^n) than **1a** (n = 1.01 and m = 22.4) at 2.0% concentration supports this observation. It has already been mentioned that the highly substituted derivatives such as **1a** and **6a** have little shear-rate dependence and are sterically resistant to self-association. Therefore, differences in viscosity, even at high (2.0 %) concentrations, are probably a reflection of the shape of the polymer molecule itself. The intrinsic viscosity values for **1a** and **6a** are then the first clue to conformational differences induced by altering the glycosidic configuration of the branch. The effect on solution properties is not particularly large in magnitude, and the similarity in trends for lower-d.s. samples for all series indicate that other associative forces which dominate resultant properties come into play at 2.0 % concentration.

TABLE II

Intrinsic viscosities for selected derivatives

Derivative	*Branch*	*d.s.* (±0.05)	$[\eta]^a$ (g/100 mL)	R^2	*No. of points*
1a	β-Glc	1.00	0.487	0.968	8
3a	β-GlcA	1.00	2.63	0.998	10
6a	β-Glc	1.00	1.46	0.947	8
7a	β-Gal	1.00	0.725	0.833	8
7b		0.86	2.39	0.931	8
7d		0.32	5.41	0.944	10

[a] Determined according to the Kramer relationship (Eq. *12*).

Other interactions. — The possibility that the *N*-[2-(glycopyranosyloxy)ethyl]chitosan derivatives might exhibit behavior similar to that of seed galactomannans led us to investigate interactions between these derivatives and xanthan[15–17]. As such, mixtures of xanthan with derivatives **2a**, **2b**, **2c**, **7c**, **7d**, **6c**, and **4b** were prepared, such that the resultant solutions contained 0.25 % of xanthan, and 0.25 % of the derivative, and an overall polysaccharide concentration of 0.50 %, as described in Table II.

The interactions between xanthan and derivatives **2c**, **7c**, **7d**, and **6** resulted in the formation of gelatinous globules that excluded solvent. With **4b**, an opaque gelatinous precipitate was obtained while **2a** and **2b** provided viscous solutions. The rheometric evaluations of these mixed solutions are compared to those of 0.25 and 0.50 % (w/w) xanthan solutions and to a known synergistic mixture containing 0.25 % xanthan and 0.25 % locust bean gum (Table IV). Interestingly, the mixture of **2b** and xanthan was more viscous (*m* 1780 mPa·s) and slightly less pseudoplastic than the 0.50 % solution of xanthan (*m* 1400 mPa·s). The interaction of **2a** with xanthan produced a less viscous solution, which still had viscosity and pseudoplasticity greater than 0.25 % xanthan.

TABLE III

Qualitative observations from synergistic mixtures containing 0.25 % xanthan and 0.25 % of the respective derivative

Derivative	*Branch*	*d.s.* *(±0.05)*	*Observations*[a]
2a	β-Gal	1.00	S, V
2b		0.70	S, V
2c		0.38	G, B, X
4b	β-Lac	0.76	G, F, X
6c	α-Glc	0.38	G, B, X
7c	α-Gal	0.48	G, B, X
7d		0.32	G, B, X

[a] B, beads; F, fibrous; G, gelatinous; S, solution; V, viscous; X, excluded solvent.

TABLE IV

Power-law parameters obtained from rheological tests on synergistic mixtures at 20°

Sample	*n*	*m* *(mPa·s)*	*R^2*	*No. of points*
Xan[a] + 2a[b]	0.409	1780	0.986	24
Xan[a] + 2[b]	0.478	605	0.974	30
Xan[a] + LBG[c]	0.402	1670	0.965	23
Xan (0.5 %)	0.397	1400	0.946	22
Xan (0.25 %)	0.518	378	0.968	27

[a] Xanthan gum at 0.25 % in the mixture. [b] Derivatives (**2a** or **2b**) at 0.25 % in the mixture. [c] Locust bean gum at 0.25 % in the mixture.

Thus, in the first case, an appreciable interaction effect is seen, resulting in viscosity greater than an equivalent concentration of xanthan. The latter case indicates that a small interaction is taking place, resulting in a lower n and larger m, than for the 0.25% xanthan solution. The locust bean gum–xanthan synergistic interaction gave a solution having a similar viscosity and pseudoplasticity as the mixture of **2b** and xanthan.

The origin of the interaction between the derivatives prepared in this study and xanthan gum is probably the result of an ionic interaction between the carboxylates of xanthan and the amine groups on the chitosan derivatives. This hypothesis is supported by reports of the formation of precipitant polyelectrolyte complexes upon mixing *O*-(carboxymethyl)cellulose and chitosan. Thus, derivatives having low d.s. permit access of the xanthan branch (bearing the carboxylate) to the free amino groups, causing a precipitate. The higher-d.s. samples sterically restrict the extent of ionic interaction and yield viscous solutions.

This observation opens up a range of opportunities for viscosity modification using mixed solutions of ionic polymers where the intermolecular ionic interactions can be controlled. As such, modified chitosans could be mixed with other anionic polysaccharides or polymers to generate viscous solutions with desirable properties.

These results also provide some insight into the behavior exhibited by the acidic and salt forms of the glucosiduronic acid derivatives **3a** and **b**. It is reasonable to expect that ionic interaction causes precipitation of high-d.s. derivatives in the acid form, but at lower d.s. values, decreased interaction could yield solutions or gels. These ionic cross-linking attractions are removed when the derivatives are in the carboxylate form.

CONCLUSIONS

A number of relationships have been identified between the solution properties of the chitosan derivatives described here and their structural variation. A series of derivatives bearing neutral monosaccharide branches showed that the solution viscosity varied inversely with degree of branching. It is postulated that this relationship follows a third-order polynomial, and comes about as the result of a complex balance of the steric interactions of the branches and a tendency toward backbone organization. Larger substituents, as exemplified by the lactosyl derivatives in this study, cause greater disruption of the backbone conformation.

The effect of substituents on macroscopic viscosity was paralleled by the effect on intrinsic viscosity. This supports the argument that the backbone conformation changes with degree of substitution, with high levels of substitution resulting in a more-random organization, while low d.s. allows a more-extended helical backbone configuration such as that of native chitosan.

It is shown that ionic interactions have a dramatic influence on solution properties, as demonstrated by the pH-dependent ionic "cross-linking" of the glucuronic acid derivatives. The solution properties of these derivatives have some similarity to those of alginate, although, calcium-induced gelation did not occur. Ionic interaction was also observed between chitosan derivatives and xanthan gum, and these interactions varied for the different branched derivatives tested. This result indicates that the kind and extent of modification provides some control over these ionic interactions.

Overall, the results demonstrate the viability of preparing a family of related structures in order to evaluate structure–property relationships. While the trends established for these derivatives may not be generally applicable to all branched polysaccharides, they should be useful for gaining insight into the properties of certain families of polysaccharides, particularly those having a β-(1→4)-glucan type backbone.

EXPERIMENTAL

Materials. — Chitosan derivatives were prepared as outlined in the accompanying report[9]. Xanthan gum (Keltrol), sodium alginate (Keltone), and locust bean gum were obtained from the Kelco Division of Merck and Co., Ltd. *O*-(Hydroxyethyl)-cellulose (medium viscosity, 4500–6500 mPa·s, 2.0 % solution) was purchased from Polysciences, Inc.

Steady-shear viscometry. — Polysaccharide solutions for viscometry were prepared by dissolving the sample in distilled water (5.0 mL) containing 50 p.p.m. sodium benzoate as stabilizer. Typically 2.0 % (w/w) solutions of all synthetic derivatives were prepared, except where otherwise indicated. Commercial polysaccharide derivatives were prepared in a similar manner, at concentrations of 1.0 and 2.0 %. All samples were given at least 24 h to disperse, with intermittent mixing on a Vortex–Genie test-tube mixer. Any samples that contained entrapped air bubbles were centrifuged on a bench-top serum centrifuge for 30 min.

The steady-shear viscometric measurements were performed on a controlled-stress rotational viscometer (Visco-Elastic Analyzer, Sangamo Transducers, Bognor Regis, United Kingdom) with truncated cone and plate fixtures (*d* 50.0 mm, α 2.5°, gap 90 μm). A controlled-temperature glycol bath under the plate provided temperature control. All measurements were recorded at 20.0° ($\pm$ 0.2°). The gap setting was zeroed with no sample present by lowering the cone fixture until contact was just made with the plate. The cone fixture was then raised to allow sample loading.

A sample solution of 1.5 mL was loaded into a syringe with an 18 gauge needle, or a Pasteur pipette for very viscous samples. The sample was discharged onto the centre of the plate, taking care to avoid the formation of air bubbles. The cone fixture was lowered onto the sample to the desired 90 μm gap setting. The sample was given 5 min to equilibrate to 20.0 ± 0.5°, as verified by measurement with a thermocouple. The sample was then stepped through a series of increasing torque settings, applied to the rotating cone fixture, typically from 0.1 to 60 g·cm. For each torque setting, the resultant angular velocity (radians·s^{-1}) was recorded on a strip chart, until the equilibrium value was reached (within 30 s for the majority of samples). When either the maximum torque (60 g·cm) or maximum angular velocity (100 radians·s^{-1}) was approached, the torque was stepped through a similar decreasing series, and the angular velocity was recorded. Duplicate measurements were performed on all samples and the data were pooled. Three Newtonian standard oil samples were also measured using this technique, in order to calibrate the torque settings over the full range of observed viscosities.

Shear stress (σ) is related to torque (T) according to Eq. *3*:

$$\sigma = \frac{3T}{2\pi r^3} \tag{3}$$

where T is torque and r is radius; and shear rate ($\dot{\gamma}$) to angular velocity (ω) according to Eq. *4*:

$$\dot{\gamma} = \frac{\omega}{\tan \alpha} \tag{4}$$

Substitution of values from cone geometry can provide shear stress and shear rate factors as seen in Eq. *5* and *6*:

$$\sigma = 2.996.7T \quad (\text{mPa}) \tag{5}$$
$$\dot{\gamma} = 22.92\,\omega \quad (\text{s}^{-1}) \tag{6}$$

Apparent viscosity will then be given by Eq. *7*:

$$\eta = (130.8)\frac{\text{T}}{\omega} \quad (\text{mPa·s}) \tag{7}$$

Corrected torque values (T_{corr}) were calculated from standard oil measurements by rearranging Eq. *7*, to give:

$$T_{\text{corr}} = \frac{\eta_{\text{oil}}\omega}{130.8} \tag{8}$$

where η_{oil} is the known standard oil viscosity, and ω was the measured angular velocity. Corrected torque values and determined angular velocities provided shear stress, shear rates, and apparent viscosities from Eq. *5*, *6*, and *7*. The logarithms of shear stress and shear rate were then calculated. Linear regression of a double-logarithmic transform of Eq. *2a* gave power-law parameters according to Eq. *9*:

$$\log \sigma = \log \text{m} + n \log \dot{\gamma} \tag{9}$$

In order to examine the fit of the power-law to the data, rheograms of steady-shear viscometric data were plotted on logarithmic coordinates as apparent viscosity *vs.* shear rate.

Intrinsic viscosity. — Solutions of 0.075, 0.050, 0.025, and 0.010 % (w/w) were prepared by dilution of 0.10 % w/w stock solutions (100 mg/100 mL) for use in intrinsic viscosity determinations. The solutions were loaded into a Cannon–Fenske capillary viscometer, according to standard procedures[19], and the viscometer was placed in a temperature-controlled jacket and allowed to equilibrate to 25 ± 0.5° for 10 min. Duplicate determinations of efflux time were recorded for each solution. Cannon–Fenske No. 50 or 100 viscometers were used in order to keep efflux times in the optimal 200–800 s range. The viscometers were calibrated with water and standard oil (7.798 mPa·s at 25°) to give the constant k according to Eq. *10*:

$$\eta = k_1 t\pi \tag{10}$$

where t is efflux time and π is density. From Eq. *10*, viscosities for all sample solutions were determined and used to calculate relative viscosity (η_{rel}) according to Eq. *11*:

$$\eta_{\mathrm{rel}} = \frac{\eta}{\eta_s} \tag{11}$$

where η_s is the solvent viscosity. Intrinsic viscosities $[\eta]$ were obtained according to the Kraemer equation:

$$\ln(\eta_{\mathrm{rel}}/c) = [\eta] + k_1'[\eta]^2 c \tag{12}$$

where c is concentration (g/100 mL) and k_1' is a constant. Linear regression of $\ln(\eta_{\mathrm{rel}}/c)$ against concentration provided intrinsic viscosities for the sample solutions.

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