Table I
Values of the Quantity $1 + 2c - \tilde{S}^{-1}(K)$ from the Numerical Work of Maeda[7] Compared with Those from Eq 8 with G Neglected and G Taken into Account

			eq 8	
scaled density	$kL = 2K$	numerical	$G = 0$	$G \neq 0$
$c = 0.04$	1	0.0022	0.0022	0.0022
	2	0.0083	0.0082	0.0083
	4	0.0272	0.0262	0.0272
	8	0.0542	0.0514	0.0540
	15	0.0661	0.0640	0.0659
$c = 0.4$	1	0.0218	0.0218	0.0218
	2	0.0831	0.0822	0.0830
	4	0.2721	0.2621	0.2716
	8	0.5417	0.5138	0.5404
	15	0.6612	0.6399	0.6590
$c = 4$	1	0.2318	0.2176	0.2182
	2	0.8745	0.8216	0.8304
	4	2.7961	2.6208	2.7161
	8	5.4337	5.1384	5.4037
	15	6.6174	6.3992	6.5896

$= \tilde{S}^{-1}(0)$ related to the osmotic compressibility.

It is important to note that $\tilde{S}(K)$ is a monotone increasing function of K. This implies that the oscillations in $\tilde{S}(K)$ found in experiments[11,12] on TMV and fd virus in salt-free solutions can be explained only by incorporating third-order and higher order virial terms into the present theory. A stringent test of the structure factor derived here and in refs 5–7 requires experiments on very slender rods like schizophyllan and fd virus (but in excess salt) for which the second virial approximation is more readily justified.

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(14) Using a variational principle together with a trial function independent of variational parameters may almost appear a contradiction in terms. But for a Schwinger principle it so happens that it is not. Indeed, its derivation proceeds in two stages (see, e.g., ref 10): (a) a first principle for $S(\mathbf{k})$ is written in terms of a trial function $\chi(\mathbf{k})$; (b) $\chi(\mathbf{k})$ is set equal to $C(\mathbf{k})\cdot\varphi(\mathbf{k})$, where the variational parameter $C(\mathbf{k})$ is obtained by minimizing or maximizing S. In our calculation the choice $\varphi(\mathbf{k}) = s_{\mathbf{k}}(\mathbf{u})$ amounts to $\chi(\mathbf{k}) = C(\mathbf{k})s_{\mathbf{k}}(\mathbf{u})$, which is of course a nontrivial trial function.

Communications to the Editor

Synthetic Glycoconjugates: Simple and Potential Glycoprotein Models Containing Pendant *N*-Acetyl-D-glucosamine and *N,N'*-Diacetylchitobiose

Oligosaccharide chains of glycoconjugates are important biopolymers not only as carriers of information in cell–cell interactions but as markers of cellular differentiation, aging, and malignant alteration. Synthetic carbohydrate polymers having pendant sugar residues are of great interest as artificial glycoconjugates from biochemical and medical aspects. In fact, as a result of increasing needs for synthetic carbohydrate polymers for medical use, there have been several examples of the preparation of sugar–acrylamide copolymers.[1-4]

To mimic and utilize the unique molecular recognition nature of oligosaccharide chains effectively, our attention is now directed to the design and preparation of new types of "pseudoglycoproteins" containing the appropriate spacer-arm structure between the sugar moiety and the main chain of copolymers. Pseudoglycoproteins as simple models of glycoproteins will provide simplified and useful information about complex functions of the saccharide region. Moreover, the introduction of a suitable spacer-arm moiety will permit flexibility of sugar side chains and thereby accessibility to the active sites, the regulation of the contents of carbohydrate monomers, and molecular weights of the polymers. This paper deals mainly with a simple and convenient method for the preparation of carbohydrate monomers based on amino sugars closely related to the invariant "core" structure of N-linked type glycoproteins with an effective spacer-arm function.

Table I
Polymerizations of Carbohydrate Monomers and Acrylamide

carbohydr monomer	monomer ratio[a]	total yield, %	polym compos[a]	sugar content, wt %	$[\alpha]_D$, deg	η_{inh},[b] dL/g
6	1:4	46.1	1:12	23.5	−6.2	0.27
6	1:10	57.4	1:42	8.0	−4.1	1.15
7	1:4	61.9	1:9	29.6	−9.6	0.43
7	1:10	59.0	1:31	11.0	−4.5	1.26
8	1:4	65.8	1:8	34.6	−11.4	0.34
8	1:10	75.6	1:28	12.5	−7.6	1.03
9[c]						
12	1:4	54.8	1:8	46.1	−11.9	0.31
12	1:10	76.0	1:23	23.1	−6.4	1.02

[a] Ratio of carbohydrate monomer and acrylamide. [b] In H_2O at 25 °C. [c] Insoluble in water.

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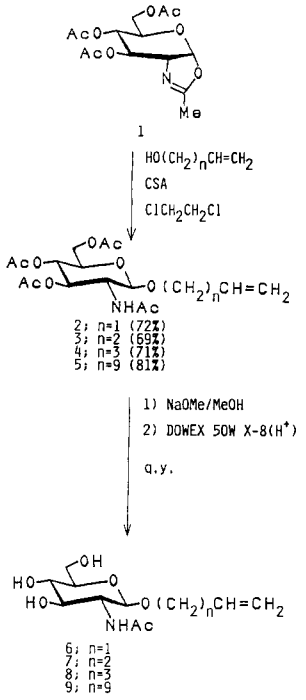
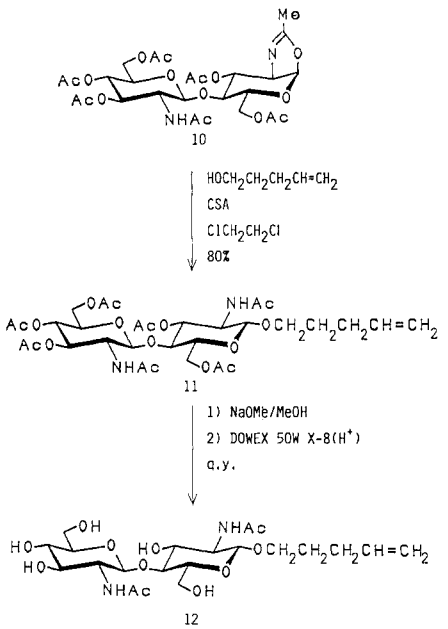
Table II
^{13}C Chemical Shifts of Copolymers Having Pendant *N*-Acetyl-D-glucosamine and *N,N'*-Diacetylchitobiose (in ppm from DSS)

compds	C-1	C-2	C-3	C-4	C-5	C-6	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′
copolymer 8	104.3	58.2	76.4	72.8	78.5	63.5						
copolymer 12	103.7	57.7	75.2	82.3	77.2	62.9	104.1	58.3	76.2	72.5	78.6	63.3

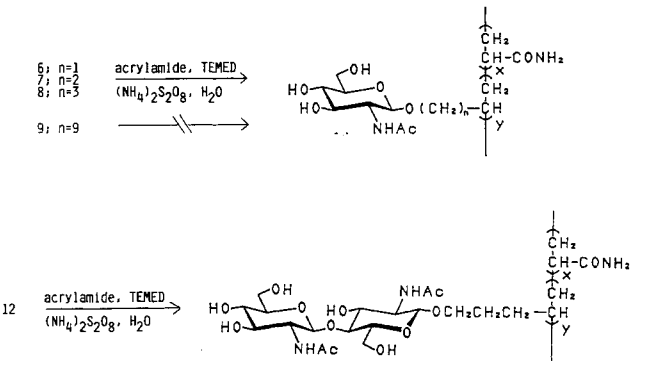
Scheme I



Scheme II



Scheme III



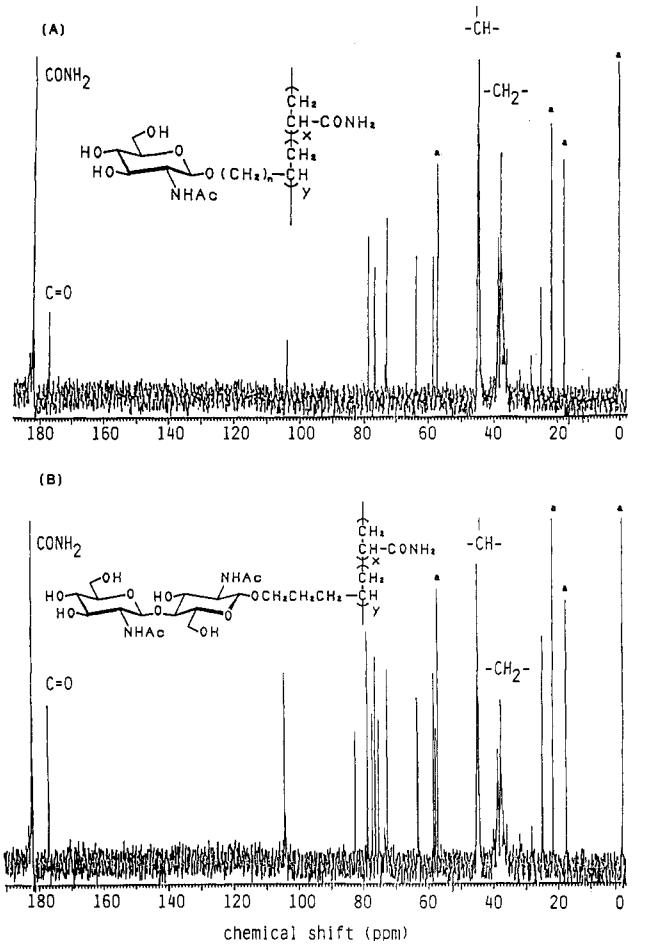


Figure 1. ^{13}C NMR spectra of the polymers measured in D_2O at 50 °C. a indicates 2,2-dimethyl-2-silapentane-5-sulfate (DSS). (A) *x*:*y* = 1:8, (B) *x*:*y* = 1:8.

An oxazoline derivative **1** (Scheme I), prepared by the trimethylsilyl trifluoromethanesulfonate (TMSOTf) method[5] from 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-glucopyranose, was allowed to react with polymerizable alcohols such as 2-propen-1-ol, 3-buten-1-ol, 4-penten-1-ol, and 10-undecen-1-ol in the presence of 10-camphorsulfonic acid as the promoter under a nitrogen atmosphere at 90 °C for 2 h to give the corresponding β-glycosides **2**–**5** in high yields.[6] They were then deacetylated by the Zemplen method to give monomers **6**–**9**, respectively, in quantitative yields.[7] The same procedure was successfully applied for the synthesis of *N,N'*-diacetylchitobiosyl monomer **12** from the readily available oxazoline derivative **10**.[8] Their structures were elucidated by elemental analyses and their ^{1}H and ^{13}C NMR spectra.

Radical copolymerizations of these monomers with acrylamide were carried out in deionized water in the presence of *N,N,N',N'*-tetramethylethylenediamine and ammonium peroxodisulfate. The reaction proceeded efficiently at room temperature. After 2 h, the viscous solution was diluted with 0.1 M pyridine–acetic acid buffer (pH 5.1), dialyzed, and freeze-dried to give water-soluble copolymers in 46.1–75.6% yields. The carbohydrate contents of the

copolymers were determined by integration of the signals due to methine (2.2 ppm) and *N*-acetyl protons (2.0 ppm) in the 270-MHz ^{1}H NMR spectra and also by the modified Park–Johnson colorimetric method.[9]

The results of copolymerization are shown in Table I together with physical data. The influence of the spacer-arm length on polymerization behavior was evident, and the amount of incorporated carbohydrate increased with increasing spacer-arm length except in the case of undecylenyl glycoside **9** owing to the poor solubility in water. Since copolymerization of the pentenyl glycoside **8** with acrylamide gave the polymer containing about 35 wt % of the *N*-acetyl-D-glucosamine unit in the highest yield, a commercially available 4-penten-1-ol[10] can be regarded as an excellent and convenient polymerizable aglycon of carbohydrate monomers. *N,N'*-Diacetylchitobiose was also successfully incorporated into the macromolecule by using the pentenyl group in a similar manner, and the sugar contents could be controlled at will. Fully assigned ^{13}C NMR spectra of copolymers in D_2O are shown in Figure 1 and Table II. The spectra show characteristic signals attributed to the ring carbons of sugar residues besides the carbons of polyacrylamide.

The synthetic strategy described here has numerous advantages for the preparation of these types of synthetic glycoconjugates with potential application to biochemical or biomedical systems. For instance, the pentenylated amino sugars **8** and **12** easily preparable in high yields possess a somewhat better polymerizability (54.8–76.0%) than the allyl or butenyl derivatives (46.1–61.9%). The sugar contents in the macromolecules can be regulated at will as the needs of the case demand. The use of a pentenyl group as a polymerizable aglycon seems to be a simpler and more convenient method than those previously published[1-4] in view of the easiness of the synthetic procedure of monomers and high polymerization yields. Moreover, unique pseudoglycoproteins may possibly be synthesized by extending the sugar moieties to include more complex oligosaccharide chains containing a reducing *N*-acetyl-D-glucosamine, such as mannosylchitobiose derivatives, fucosylchitobiose derivatives, and *N*-acetyllactosamine and its derivatives related to tumor-associated antigens.[11] Detailed investigation of the interaction between the glycoprotein models and lectins is now under way, and the results will be reported in the near future.

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