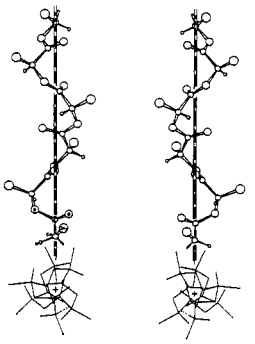

poly(L-lactide) poly(D-lactide)

Figure 3. Chain models of poly(L-lactide) and poly(D-lactide).

the two different helical chains in solution where molecular motion is sufficiently great. More detailed studies on this novel stereopolymeric complex formation will be published in the near future.

Registry No. Poly(L-lactide)/poly(D-lactide) complex, 106989-12-2; poly(D-lactide) (SRU), 26917-25-9; poly(L-lactide) (SRU), 26161-42-2.

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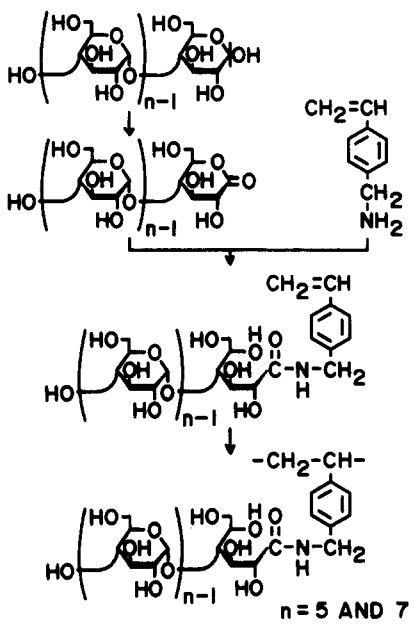
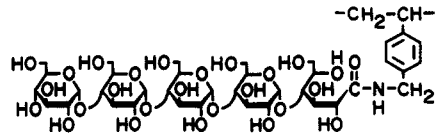
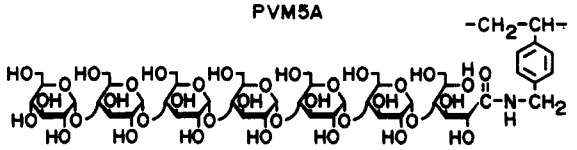
Maltopentaose- and Maltoheptaose-Carrying Styrene Macromers and Their Homopolymers

Polystyrene derivatives with maltopentaose and maltoheptaose substituents on each benzene ring, which are termed PVM5A and PVM7A, respectively, have been synthesized. These oligosaccharide-carrying polystyrenes are a new type of homopolymer with a graft of uniform length in every repeating structural unit. In each unit, the reducing end of the hydrophilic oligosaccharide is connected via an amide linkage with the hydrophobic *p*-vinylbenzylamine main chain. The synthetic route is shown in Scheme I. Each of maltopentaose ([*O*-α-D-glucopyranosyl-(1→4)]$_4$-D-glucopyranose, M5) and maltoheptaose ([*O*-α-D-glucopyranosyl-(1→4)]$_6$-D-glucopyranose, M7) was oxidized to the corresponding lactone, which was then coupled with *p*-vinylbenzylamine. The resulting well-defined water-soluble amphiphilic macromonomer, *N*-(*p*-vinylbenzyl)-[*O*-α-D-glucopyranosyl-(1→4)]$_{n-1}$-D-gluconamide (VM5A for $n = 5$ and VM7A for $n = 7$), was polymerized with a radical initiator in water. This is the first report on well-defined synthetic polymers with oligosaccharides of intermediate chain length as the pendant group.

Scheme I







Complex oligosaccharide chains of glycolipids and glycoproteins protrude from the surface of cell membranes and play an important role in biological recognition events.[1] Synthetic polymers endowed with informational oligosaccharides, even with commercially available simple ones, are of interest in connection with application for biomedical and separation materials. A few papers have been reported on di- and trisaccharide-carrying polymers.[2-8] Two synthetic methods are available for this purpose: (a) reaction of oligosaccharides onto polymeric substances[2,3] and (b) synthesis and polymerization of vinyl

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Table I
Polymerization of N-(p-Vinylbenzyl)-[O-α-D-glucopyranosyl-(1→4)]$_4$-D-gluconamide (VM5A) and N-(p-Vinylbenzyl)-[O-α-D-glucopyranosyl-(1→4)]$_6$-D-gluconamide (VM7A) at 60 °C

	monomer							[η]^b	
	g	mmol	$K_2S_2O_8$, mol %	water, mL	time, h	yield, %	$[\alpha]^{25}_D$,^{a} deg	in H_2O	in Me_2SO
VM5A	0.96	1	0.2	1.2	11	69	+146	0.28	0.97
VM7A	1.28	1	0.25	1.5	18	71	+152	0.47	0.91

^{a} 1 g/100 mL in H_2O. ^{b} At 25 °C; calculation was made with the concentration expressed in g/100 mL.

and diacetylene compounds having an oligosaccharide substituent.[4-8]

Recently, we reported that the synthetic route shown in Scheme I was a convenient, high-yield procedure for preparing mono-, di-, and trisaccharide-carrying polystyrenes.[9,10] It was found[10-12] that the pendent oligosaccharides of these polymers function as specific recognition markers for proteins and cells. Especially, the galactose-specific interaction between the lactose-carrying polymer and liver cells (hepatocytes) is of importance.[11,12] Hepatocytes, which usually have only a limited viability in vitro, were found to adhere and survive in culture dishes that were coated with lactose-carrying polystyrene.

In the present investigation, we adopted maltooligosaccharides with a uniform degree of polymerization (DP = 5 and 7) and purity greater than 99.9%. Each oligosaccharide was oxidized with potassium hypoiodite in water at room temperature and the resulting potassium oligosaccharide aldonate was neutralized by passing through a column containing Amberlite IR-120 (H^+). Freeze-drying of the solution gave the corresponding lactone as a white powder in an almost quantitative yield.

Each oligosaccharide lactone was dissolved in ethylene glycol and heated with 1.0—1.5 mol equiv of p-vinylbenzylamine at 70 °C for 8–13 h. Compared with the reactions of di- and trisaccharide lactones, prolonged heating was required. The product was precipitated in acetone, chromatographed on silica gel (eluent: acetone/methanol/water = 8/3/2 volume ratio), and freeze-dried from water. The yield was 70–80%. $[\alpha]^{25}_D$ of VM5A: +157° (1 g/100 mL in water); $[\alpha]^{25}_D$ of VM7A: +148° (1 g/100 mL in water).

Polymerization of VM5A and VM7A was carried out in water with potassium peroxydisulfate as initiator at 60 °C (Table I). Polymerization proceeded homogeneously leading to a viscous solution. The solution was poured into methanol, and the precipitated polymer was dissolved in water, dialyzed, and freeze-dried. The polymer obtained was a white powder that was soluble in water and dimethyl sulfoxide (Me_2SO).

Figure 1 shows the ^{13}C NMR spectrum of PVM7A in Me_2SO-d_6 wherein the assignment of the signals was made by comparison with ^{13}C NMR spectra of glucose-, maltose-, maltotriose-, and maltopentaose-carrying homologues. The C-2, C-3, and C-5 resonances of the central five glucopyranosyl residues appeared distinguishably as the signals g_2, g_1, and g_3, respectively, which corresponded to those signals of amylose.[13] The chemical shift data are as follows (primes and doulbe primes designate the central α-D-glucosyl residues and the terminal one, respectively): 171.9, C=O; 144, 136, and 127, phenyl; 100.3 and 100.1, C-1′ and C-1″; 82.2, C-4; 79.1 and 78.6, C-4′; 73.0, C-3′; 71.9, C-2′; 71.5, C-5′; 70.1, C-4″; 62.5, C-6; 60.9 and 60.4, C-6′ and C-6″. When D_2O was used as the solvent, a benzylmethylene signal at 42.8 and main-chain methylene and methyne signals around 40–43 ppm were also detected. The signals of the main chain methylene and methyne, phenyl, and benzylmethylene carbons were broad, and hence stacking of the phenyl groups and small mobility of the main chain

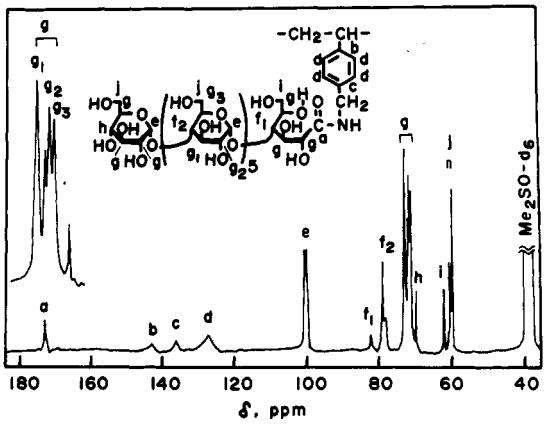

Figure 1. ^{13}C NMR spectrum of PVM7A: solvent, Me_2SO-d_6, 7.5%; 80 °C; 26 200 scans; 5-mm-i.d. tube; Me_4Si standard; 50 MHz.

are suggested.

The intrinsic viscosities determined in Me_2SO were higher than 0.9, but those determined in water were only about 30–50% of those in Me_2SO. As suggested previously,[9,10] we assume that the low viscosity in water reflects a tightly coiled micellar conformation of the polymer, which is attributable to their amphiphilic structure.

Polystyrene derivatives with one, two, three, five, and seven α-D-glucopyranosyl residues on each benzene ring have been prepared so far. Effects of the chain length of these polymers on biological recognition ability, binding of organic solutes in water, and solution properties are of interest. We also except that a new field of oligosaccharide-grafted polystyrenes will be developed if the present procedure is applicable to more complex and higher oligosaccharides and polysaccharides.

Acknowledgment. We thank Nihon Shokuhin Kako Co., Ltd. for supplying maltopentaose and maltoheptaose.

Registry No. PVM5A, 106989-25-7; PVM7A, 106989-27-9; VM5A, 106989-24-6; VM7A, 106989-26-8; maltopentaose, 34620-76-3; maltoheptaose, 34620-78-5; maltopentaose lactone, 107035-67-6; maltoheptaose lactone, 77893-27-7; p-vinylbenzylamine, 50325-49-0.

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CORRECTIONS

Graeme Moad,* David H. Solomon, Stanley R. Johns, and Richard I. Willing: Fate of the Initiator in the Azobis(isobutyronitrile)-Initiated Polymerization of Styrene. Volume 17, Number 5, May 1984, p 1094.

In Table II, the last two entries should read

compd	carbon	shift, δ
8	$(CH_3)_2CHC(O)NH-$	35.6
9	$(CH_3)_2CHC(O)NH-$	35.6

The signals labeled a and b in Figure 2 are mislabeled. The last sentence in the legend should read "The signals at a and b are assigned to copolymerized MAN and to the 'normal end group' respectively." Reference 8 should be: Moad, G.; Solomon, D. H.; Johns, S. R.; Willing, R. I. *Macromolecules* **1982**, *15*, 1188.

Gérard Charlet and Derek G. Gray*: Solid Cholesteric Films Cast from Aqueous (Hydroxypropyl)cellulose. Volume 20, Number 1, January 1987, p 33.

Four sentences should be added to the end of the section entitled **Dynamic Mechanical Properties**. They read

It also explains the persistence of order in the polymer cast from its solutions. Upon drying, the cholesteric structure "freezes" at the concentration where the chain mobility suddenly decreases, i.e., where intermolecular bonds form. The static tensile and dynamic mechanical properties of HPC films prepared under various conditions are reported in an article published during the preparation of this manuscript.[22] The results present the same general features, and the transition around 110 °C is ascribed to the rotation of anhydroglucose rings, through a decrease of hydrogen bonding.