yield. δ H_α = 8.41 (J_{HW} = 13.7 Hz), δ C_α = 244.9 (J_{CW} = 200 Hz, J_{CH} = 114 Hz) in C_6D_6. Anal. Calcd for $WC_{25}H_{39}NO_2F_6$: C, 43.94; h, 5.75. Found: C, 43.67; H, 5.60. (b) *cis*-3-Hexene (45 μL, 10 equiv) was added to a solution of 25 mg of W(CH^{t}Bu)(NAr)[$OCMe_2(CF_3)$]$_2$ in 1.0 mL of C_6D_6. The solution was heated for 5.5 h at 45 °C. By ^{1}H NMR the ratio of W(CHEt)(NAr)[$OCMe_2(CF_3)$]$_2$ to W(CH^{t}Bu)(NAr)[$OCMe_2(CF_3)$]$_2$ was 4.4:1. The Hα signal in the former is found at 8.77 ppm (t, J_{HH} = 6.3 Hz).

(16) Metathesis of 500 equiv of *cis*-2-pentene in pentane is complete (at equilibrium) in <5 min. The details of reactions of W(CHEt)(NAr)[$OCMe_2(CF_3)$]$_2$ with ordinary olefins will be reported separately.

(17) W(CH^{t}Bu)(NAr)(O^{t}Bu)$_2$ was prepared by adding 407 mg of LiO^{t}Bu (5.08 mmol) to 1.50 g of W(CH^{t}Bu)(NAr)(dme)Cl_2[6] in 60 mL of ether at −30 °C. The solution was warmed to 25 °C and stirred for 45 min. LiCl was filtered off, and the ether removed in vacuo. Recrystallization of the crude product from minimal pentane at −30 °C gave W(CH^{t}Bu)(NAr)(O^{t}Bu)$_2$ as a bright yellow solid in 60% yield. δ H_α = 8.01 (J_{HW} = 12.5 Hz), δ C_α = 236.5 (J_{CW} = 201 Hz, J_{CH} = 110 Hz) in C_6D_6. Anal. Calcd for $WC_{25}H_{45}NO_2$: C, 52.18; H, 7.88. Found: C, 51.67; H, 7.67.

(18) A solution of norbornene (33 mg) in 500 μL of toluene-d_8 was added to a rapidly stirred solution of W(CH^{t}Bu)(NAr)(O^{t}Bu)$_2$ (20 mg) in 500 μL of toluene-d_8. An ^{1}H NMR spectrum of the resulting living oligomer is shown in Figure 1. The initial trans:cis ratio is 1.7. After 24 h it is 2.0, and after 8 days it is 3.0. Since the living oligomer decomposes slowly ($t_{1/2} \simeq 6$ days) or possibly is simply hydrolyzed by traces of water, it is unclear what catalyst is responsible for cis/trans isomerization.

(19) The reactions were done in C_6D_6 at 25 °C at a tungsten concentration of ~0.03 mM. By NMR the reaction was complete in minutes. Wittig-like reactions of alkylidene complexes were first noted with Ta(CH^{t}Bu)($CH_2{}^tBu)_3$[20] and titanium–methylene complexes.[21] Recently, five coordinate tungsten alkylidene complexes have been reported to behave similarly.[22] What we believe to be W(O)(NAr)(O^{t}Bu)$_2$ and largely *trans*-^{t}BuCH=CHPh are formed upon reaction of W(CH^{t}Bu)(NAr)(O^{t}Bu)$_2$ with benzaldehyde. W(O)(NAr)(O^{t}Bu)$_2$ was prepared by an independent route and shown to be identical with the product of the reaction shown in eq 1.

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Structure of a Poly[(1→4)-α-D-galactosamine anhydride] Studied by X-ray Diffraction Coupled with Conformational Analysis

The configurational difference between D-glucose and D-galactose lies only in the geometrical position of the hydroxyl group with respect to the pyranose ring at C(4) when both monosaccharides take the common conformation of C1, axial for the latter and equatorial for the former. When these sugars are polymerized with (1→4) linkages, however, it is expected that the resultant polysaccharides should show an observable conformational difference. On the other hand, changing the hydroxyl group at C(2) to a primary amino group (NH_2), as in D-glucose to D-glucosamine or in D-galactose to D-galactosamine, may not cause marked conformational changes in the corresponding polysaccharides (D-glucan and poly[D-glucosamine], or D-galactan and poly[D-galactosamine]), since both OH and NH_2 are at the equatorial position with respect to the pyranose ring and their volumes are not very different. In practice, chitosan, poly[(1→4)-β-D-glucosamine], takes a conformation similar to that of cellulose, (1→4)-β-D-glucan. Both are extended twofold helices.[1]

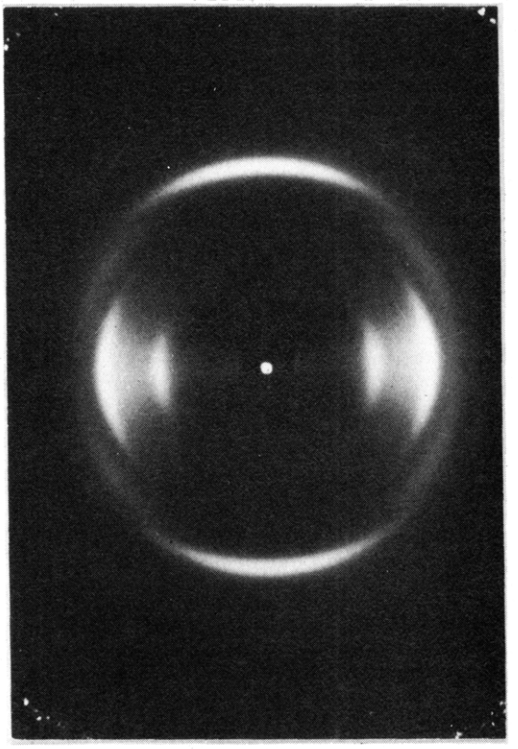

Figure 1. X-ray diffraction pattern of the poly[(1→4)-α-D-galactosamine] fiber annealed in water at 140 °C. Fiber axis is vertical.

Among polysaccharides having a galactopyranosyl backbone, pectic acid, poly[(1→4)-α-D-galacturonic acid], has been extensively studied by X-ray diffraction. Palmer et al. found that sodium pectate,[2] pectic acid, and pectinic acid[3] all take similar threefold helical structures having a fiber repeat of 13.1 Å. Walkinshaw and Arnott found that the chirality of the pectic acid was right handed.[4,5]

Recently, Takagi and Kadowaki extracted a (1→4)-α-D-galactosamine polymer from the culture fluid of *Paecilomyces sp.* I-1.[6] They also found that this polysaccharide had a flocculating action similar to that of chitosan on suspended soil in aqueous solution.[7]

We wish to report an X-ray fiber diffraction study coupled with an energy calculation on poly[(1→4)-α-D-galactosamine], which is the second polysaccharide having a galactopyranosyl backbone studied by X-ray diffraction. A twofold helical structure was found for the poly[galactosamine].

Poly[(1→4)-α-D-galactosamine] powder, supplied by Higeta Shoyu Co. Ltd., Chiba, Japan, was prepared as a 0.17 M acetic acid solution (0.2 g L^{-1}), which was extruded into isopropyl alcohol using a Teflon beaker[8] and allowed to stand for 5 min.[9] After drying in air the resultant fiber was immersed in 0.5 M aqueous NaOH for 10 min to make an acetate-free fiber of constant fiber length and washed

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Table I
Observed Spacings and Intensities for the Annealed Poly[(1→4)-α-D-galactosamine]

hkl	spacings, A calcd	spacings, A obsd	intensities obsd[a]
040	7.70	7.50	s
100	5.20		
060	5.13	5.03	vs
110	5.13		
120	4.93		
011	8.37	8.15	vw
101	4.46		
061	4.42	4.39	m
111	4.42		
121	4.29		
141	3.86	3.83	w
022	4.19	4.18	vs
042	3.79	3.75	vw
102	3.34		
062	3.32	3.33	m
112	3.32		
033	2.79	2.75	vw
123	2.50	2.49	w

[a] Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

Table II
Crystal Data for the Annealed Poly[(1→4)-α-D-galactosamine]

crystal system	orthorhombic
lattice parameters	
a, A	5.2
b, A	30.8
c (fiber axis), A	8.7
ρ(obsd), g cm^{-3}	1.48
no. of galactosamine residues	8
ρ(calcd), g cm^{-3}	1.53
helix parameters[a]	
n	2
h, A	4.35

[a] *n* is the number of the galactosamine residues per turn. *h* is the advance per residue along the helix axis.

with water. The fiber thus prepared was of low crystallinity. When the same fiber was annealed in water, keeping the length constant at 140 °C in a closed bomb, it showed higher crystallinity. The density was measured by the flotation method in a carbon tetrachloride–*m*-xylene solution. The X-ray diffraction patterns were recorded with a flat-film camera with a Rigaku Geigerflex X-ray diffractometer employing Ni-filtered Cu Kα radiation generated at 40 kV and 15 mA.

The fiber of poly[(1→4)-α-D-galactosamine] annealed at 140 °C showed a fiber pattern (Figure 1) that indicated high crystallinity but somewhat low orientation. Increasing the annealing temperature to 200 °C did not produce any change in the pattern, and attempts to improve the orientation, such as stretching the poly[galactosamine] film, were not successful.

In spite of its high crystallinity, there were observed only 10 reflections on 4 layer lines and (particularly important) only two equatorial spots,[10] suggesting that the unit cell had an elongated base (*ab*) plane: an orthorhombic unit cell with $a = 5.2$, $b = 30.8$, and c (fiber axis) = 8.7 Å (Tables I and II). The fiber axis length suggests a twofold helical structure for the poly[galactosamine]. The observed density (1.48 g/cm^3) and the volume of the cell (1393.4 Å^3) indicate the presence of four poly[galactosamine] chains in the unit cell. The fiber pattern did not change with variation in humidity, suggesting the absence of water molecules in the crystal.

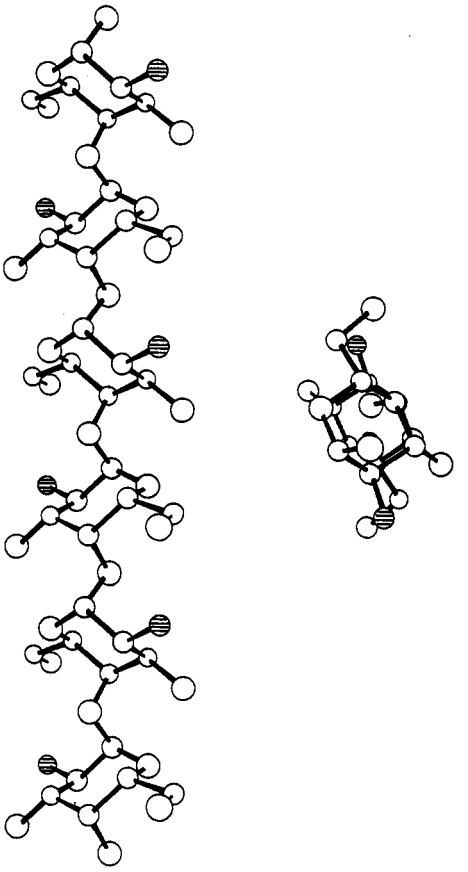

Figure 2. Twofold poly[(1→4)-α-D-galactosamine] helix, projected perpendicular (left) and parallel (right) to the chain axis. The striped balls are nitrogen atoms. All the hydrogen atoms are omitted.

It is interesting that the fiber repeat of the poly[galactosamine], 8.7 Å, is very similar to that of various pectin [poly[(1→4)-α-D-galacturonic acid]] esters, which were anticipated to take twofold helices by Palmer and Ballantyne from their powder diffraction patterns.[11] Furthermore, from circular dichroism measurements, Morris et al. postulated that pectic acid took a 2_1 conformation when complexed with calcium ion,[12] although a recent X-ray study of the complex indicated that the pectic acid retained a 3_1 helix.[5] The fiber repeat is similar to that of poly[(1→4)-α-L-guluronate], which also has a twofold symmetry.[13] This suggests that the poly[D-galactosamine] structure is essentially a mirror image of that of poly[L-guluronate] since the conformation of the pyranose ring in D-galactopyranose is C1, whereas for L-gulopyranose it is 1C.

We studied a number of possible conformations for the twofold helical conformation of the (1→4)-α-D-galactosamine, having a fiber repeat of 8.7 Å, by using the computer program PS 79.[14,15] The initial atomic coordinates of an α-D-galactosamine residue were derived from those of α-D-galactose determined by Sheldrick.[16] The atomic distance between O(1) and O(4) (virtual bond length) of our model of α-D-galactosamine is 4.53 Å, the same as that of α-D-galactose.[16] The resultant most probable conformation for the poly[galactosamine] free chain is shown in Figure 2, in which the glycosidic torsion angles are ϕ[H(1)–C(1)–O(1)–C(4′)] = −26.4° and ψ[C(1)–O(1)–C(4′)–H(4′)] = 27.8°, the angle of the glycosidic bridge oxygen τ = 115°, and the O(6) rotational state is *tg*. It takes a "kinked" twofold helical structure and is a mirror image of the poly[(1→4)-α-L-guluronate] reported by Atkins et al.[13] when only (1→4)-linked α-pyranose rings are taken

into account. The exact chain conformation, however, is under study and will be published after the final analysis of the present X-ray fiber diffraction study.

No X-ray study has been reported on (1→4)-α-D-galactan, but it would be expected to take a similar conformation to that of the present poly[galactosamine] if substituting the hydroxyl group for the amino group at C(2) does not affect the 2_1 symmetry: for example, in the case of glucopyranosyl polysaccharides, both cellulose and chitosan show 2_1 symmetry. On the other hand, substituting the carboxyl group for the hydroxymethyl at C(5) may change the conformation from 2_1 to 3_1[2-5] symmetry. Our recent conformational analysis for (1→4)-α-D-galactan[17] suggested that the galactan was able to take a twofold helical structure with a fiber repeat of 8.7 Å though the energetically most favorable conformation was a 2_1 helix having a 8.9-Å fiber repeat and that a threefold helix with a 13.5-Å fiber repeat was possible as well.

It is important to discuss the conformational difference between (1→4)-linked glucopyranose and galactopyranose polymers. Amylose, the α-D-glucan, forms a large-amplitude 6-fold helix. According to our previous conformational analysis, the energetically most stable structure of β-D-galactan is an expanded 6-fold helix.[18] On the other hand, the present poly[α-D-galactosamine] (and maybe the α-D-galactan) and common cellulose, the β-D-glucan, take ribbonlike structures, although the latter is nearly fully extended and the former is kinked. Pectic acid, poly[α-D-galacturonic acid], takes a threefold helix, but it has an h value (4.43 Å), the rise per residue along the helix axis, similar to that of the present poly[galactosamine] (h = 4.35 Å), indicating that they do not have any drastic conformational difference.

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(8) The use of a glass beaker made it difficult to remove the resultant fiber since the fiber adhered strongly to the glass.
(9) Less than 5-min immersion did not give a stable fiber while 10-min standing caused loss of fiber orientation.
(10) The fiber before annealing gave a diffuse pattern having only one equatorial reflection (d = 6.4 Å) when X-rayed at 100% relative humidity. Under vacuum a much more diffuse pattern was observed. These indicate a different polymorph, including water molecules from that of the annealed material.
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Correlation between the Glass Transition Temperatures of Polymer Mixtures and Intermolecular Force Parameters

In a previous publication[1] an equation of the following form was proposed to account for the variation of the glass transition temperatures of mixtures of poly(methyl methacrylate) (PMMA) and phenolic resins with blend compositions.

$$T_g = (W_1T_{g1} + kW_2T_{g2})/(W_1 + kW_2) + qW_1W_2 \quad (1)$$

The first term on the right-hand side of eq 1 is identical with the widely used Gordon–Taylor[2] expression, and the second term represents the effect of polymer–polymer interaction, hydrogen bonding for the blends under consideration, on T_g. Note that eq 1 reduces to an earlier equation by Jenckel and Heusch[3] when k = 1. But experimental T_g data for several mixtures can be fitted only by k values not equal to unity. Equation 1 is also different from the one used by Tsutsui et al.,[4] in which the second term is $qW_1W_2/(W_1 + kW_2)$.

Additional reports appeared recently on the use of eq 1 to represent the T_g data of polymer mixtures. Of particular interest are the results of Percec and co-workers[5,6] on blends of polymers containing electron donor and acceptor groups, for which the values of q were found to be positive in some mixtures but negative in others. Almost simultaneously Pennacchia et al.[7] also found that the T_g data for mixtures of PMMA with p-NO_2- or p-t-Bu-substituted phenolic resins could be represented by eq 1 with negative q values.

Originally, it was thought that interchain specific interaction, at least in the case of hydrogen bonding, reduced segment mobility and raised T_g in a way analogous to cross-linking and q could be regarded as a measure of such

Table I
q and k Values from T_g Data

	PMMA		PEMA	
substituent	q	k	q	k
p-hydro	44.2	0.89	42.2	1
p-methyl	41.2	0.88	44.0	1
p-*tert*-butyl	−39.4	1	−38.8	1
p-nitro	−41.9	1	−54.7	1
p-fluoro	67.9	0.87	68.2	0.89
p-chloro	44.8	1	52.4	1

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