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position themselves so as to eliminate their most severe steric interactions. Inclusion of an appropriate torsional energy potential to account for the rotation required for the helical structure would make the helix and all-trans conformations somewhat closer in energy while the trans–gauche conformation would still remain higher in energy. While bond-angle and bond-length distortions in the latter could perhaps lower the energy significantly by reducing severe steric interactions, it is unlikely that such deformations (each carrying its own energy cost) could make the conformation comparable to the lowest energy conformations available to PDHS. It should be noted that rotations about all of the C–C bonds have not yet been fully examined for their influence on the energies for these backbone conformations, nor have all possible combinations of torsion angles for the Si–C and the first C–C bond been explored. Such additional calculations are currently in progress.

In spite of the somewhat preliminary nature of the calculations, the results are in good agreement with the structures observed in X-ray diffraction studies. The lowest energy conformation, the 7/3 helix, is actually observed[11] in the crystalline structure of PDPS. At the same time, the all-trans conformation observed[6,7] in the crystalline state of PDHS is also found to have a reasonable, though somewhat higher, energy. Other spectroscopic data for PDHS also indicate[6] that the side chains are not normal to the plane of the backbone, in accord with the indicated rotations about the Si–C bonds needed to give a low energy.

The present results are not in agreement with results of earlier calculations.[10] These discrepancies are attributable to the limitations of the previous calculations cited earlier.

Perhaps the most significant finding from the energy calculations thus far is that the all-trans conformation is not the lowest energy structure for the symmetrically alkyl-substituted silane polymers. In fact, a helical structure is preferred for the isolated molecule. The calculations, in conjunction with X-ray data[6,7,11] from PDHS and PDPS, indicate that it is intermolecular interactions in the crystal that lead to the all-trans conformation. Furthermore, these results suggest that there is a critical side-chain length (about six carbon atoms) needed to provide sufficient intermolecular interaction in the solid state to force the silicon backbone out of the preferred helical conformation into the all-trans conformation in order to optimize those intermolecular side-chain interactions. This result, taken in the context of experimental data reported elsewhere, provides a framework wherein the UV absorption characteristics of these polymers can be understood.

Registry No. PDHS, 97036-67-4.

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B. L. Farmer*
Department of Mechanical and Materials Engineering
Washington State University
Pullman, Washington 99164-2720

J. F. Rabolt and R. D. Miller
IBM Almaden Research Center
San Jose, California 95120-6099

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Ring-Opening Polymerization of Norbornene by a Living Tungsten Alkylidene Complex

Careful design of isolable, well-characterized catalysts is the key to the preparation of living polymers and ultimately well-defined block copolymers by ring-opening metathesis polymerization of cyclic olefins.[3] This has been demonstrated recently in the ring-opening polymerization of norbornene by a titanacyclobutane/titanium carbene complex[4a] and by a related tantalum catalyst.[4b] These living polymer systems produce monodispersed polymer. The utility of the Ti polymerization catalyst in polymer synthesis has been demonstrated by the production of A–B–A triblock polymers.[5] Tungsten metathesis catalysts have recently been reported that are much more active than the titanium catalysts and show a greater tolerance of polar functional groups.[6–9] One of these has been shown to produce a growing alkylidene in the polymerization of norbornene.[7] Since a variety of ligand combinations is now available, we should be able to fine tune catalyst activity precisely to the point required for controlled polymer synthesis. The complex W(CH^{t}Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (Ar = 2,6-diisopropylphenyl)[6] will react rapidly with ordinary olefins to give isolable tungstacyclobutane complexes or alkylidene complexes (depending on the degree of substitution of the tungstacyclobutane ring) and will metathesize an internal olefin such as *cis*-2-pentene at a rate whose lower limit is 1000 turnovers per minute at 25 °C. Here we show that the activity of this system is dramatically altered by the choice of the alkoxide, and we can prepare a catalyst that shows all the characteristics for a living ring-opening polymerization of norbornene.

In an initial experiment W(CH^{t}Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ was allowed to react with 288 equiv of norbornene in toluene at −40 to −20 °C over several hours. Aliquots were withdrawn at intervals and the isolated polymers analyzed by GPC.[10] *All* of the samples had the same high molecular weight values ($M_n \approx 400000$; $M_w \approx 650000$; vs. polystyrene standards), indicating slow initiation followed by very rapid propagation and finally termination.[11] Analysis by ^{13}C NMR indicated $\geq 95\%$ cis double bonds.[12]

The polymerization was investigated further in a series of sealed NMR-tube experiments in toluene-d_8. The initial ^{1}H NMR spectrum obtained at −80 °C showed no catalyst or catalyst-derived signals (only monomer and polymer were observed). A constant rate of polymer formation (zero order in monomer) was observed when the polymerizations were followed at −60 °C.[13] As the reaction proceeded signals attributable to decomposed catalyst slowly in-

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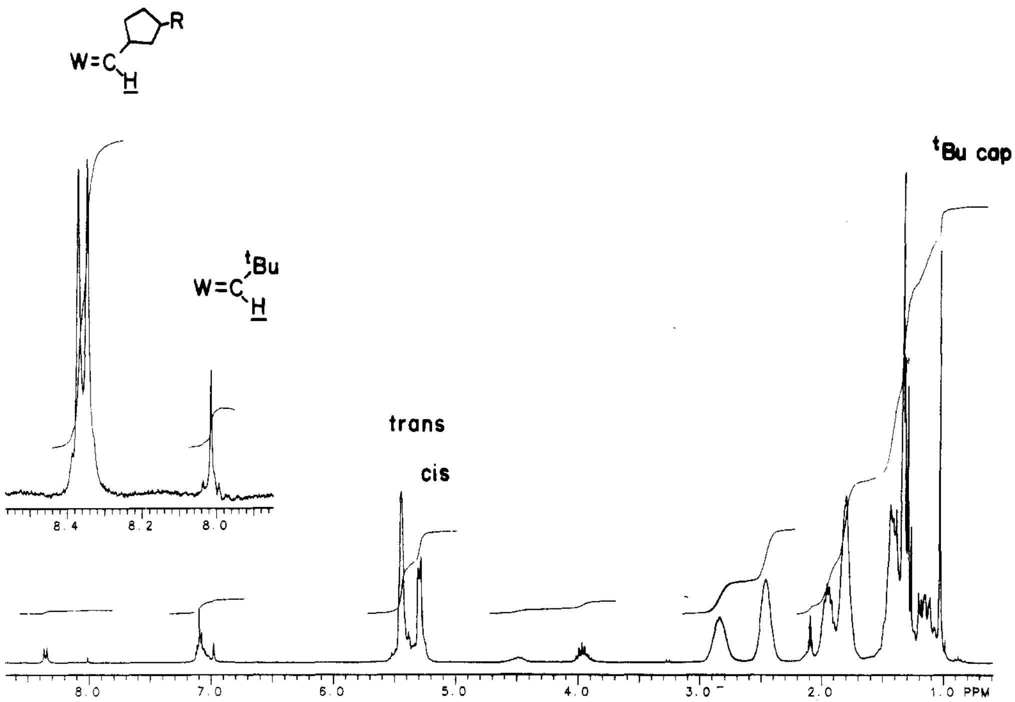

Figure 1. 300-MHz ^{1}H NMR spectrum of W[(CHC$_5$H$_8$CH)$_x$CH^{t}Bu](NAr)(O^{t}Bu)$_2$ (x_{av} = 10; δ H$_\alpha$ 8.36) prepared by adding 10 equiv of norbornene to W(CH^{t}Bu)(NAr)(O^{t}Bu)$_2$ (δ H$_\alpha$ 8.01).

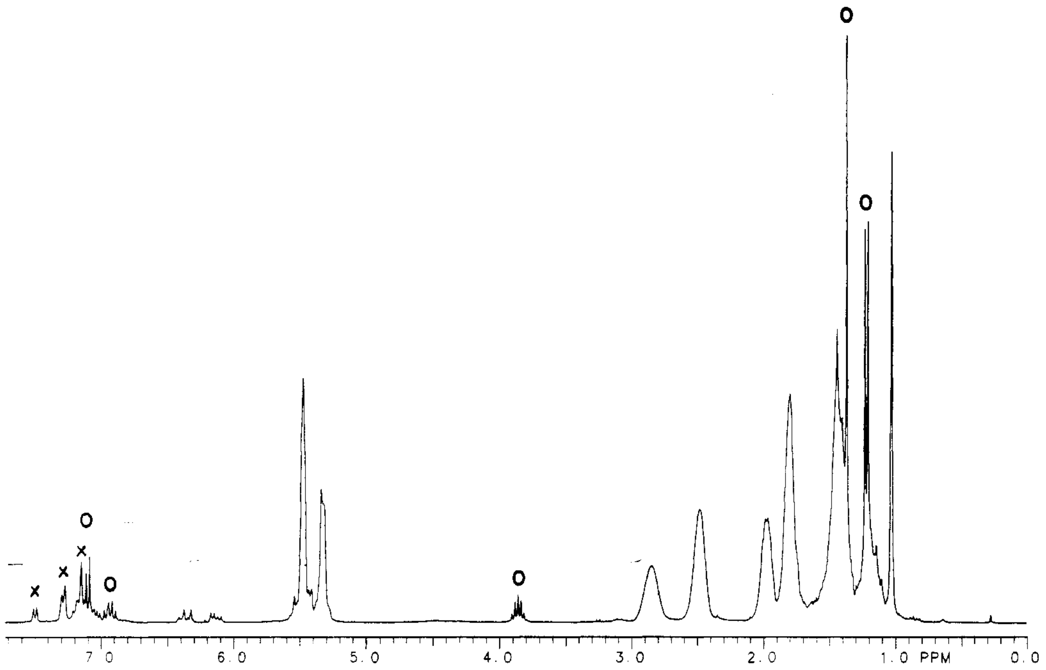

Figure 2. 300-MHz ^{1}H NMR spectrum of a mixture of benzaldehyde, PhCH(CHC$_5$H$_8$CH)CH^{t}Bu (x_{av} = 10), and W(O)(NAr)(O^{t}Bu)$_2$ (O) formed by treating W[(CHC$_5$H$_8$CH)$_x$CH^{t}Bu](NAr)(O^{t}Bu)$_2$ with benzaldehyde (×).

creased and reached maximum intensity at 100% completion.[14] As the sample warmed to room temperature, the expected doublet signal for the alkylidene proton of the growing chain appeared at 9.24 ppm (J_{HH} = 7.3 Hz). However, the intensity was only 5–10% of that to be expected if all the initial alkylidene had been transformed into the propagating alkylidene. An approximately equal amount of a signal due to the initial neopentylidene complex reappeared, but the majority of the initial tungsten complex apparently decomposed in an as yet undefined manner. At 25 °C the all cis polymer isomerized to predominantly trans over several days. GPC analyses[10] of the polymers formed at low temperature showed M_n and M_w values comparable to those obtained above. Samples allowed to isomerize to predominantly trans polymer, presumably by secondary metathesis of C=C bonds in the polymer, showed the expected increase in polydispersity. Finally, in a polymerization (74 equiv of norbornene) initiated at −80 °C, but then rapidly warmed to room temperature, much lower molecular weights (M_n = 9400; M_w = 21 000) were obtained, although the polydispersity remained high.

W(CH^{t}Bu)(NAr)[OCMe$_2$(CF$_3$)]$_2$[15a] can be prepared straightforwardly from W(CH^{t}Bu)(NAr)(MeOC$_2$H$_4$OMe)Cl$_2$.[6] It reacts slowly with *cis*-3-hexene to give W(CHEt)(NAr)[OCMe$_2$(CF$_3$)]$_2$[15b] which, like W(CHEt)(NAr)[OCMe(CF$_3$)$_2$]$_2$,[6] decomposes to the extent of at least 10% in 1 day in the absence of air and moisture.

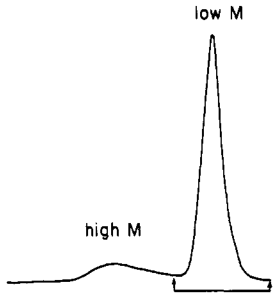

Figure 3. GPC trace (toluene, 25 °C) for polynorbornene (100 equiv) prepared by using $W(CH^tBu)(NAr)(O^tBu)_2$ as the catalyst. The peak labeled "low M" comprised between 80% and 90% of a typical sample. Analysis between the limits shown yielded the results shown in Table I.

$W(CH^tBu)(NAr)[OCMe_2(CF_3)]_2$ is a good catalyst for the metathesis and isomerization of *cis*-2-pentene[16] but is clearly considerably less active than $W(CH^tBu)(NAr)[OCMe(CF_3)_2]_2$. Ten equivalents of norbornene reacts with $W(CH^tBu)(NAr)[OCMe_2(CF_3)]_2$ to give a mixture containing ~50% $W[(CHC_5H_8CH)_xCH^tBu](NAr)[OCMe_2(CF_3)]_2$ (δ H_α = 8.78 ppm). The intensities of the signals for H_α in the initial and new alkylidene complexes (vs. an internal standard) are what is expected if there is virtually no decomposition of the new alkylidene complex in the absence of air or moisture in ~1 h. However, the cis content of the polymer decreases with time (from 1:4 to 1:2 trans:cis in 3 h), as one would expect if $W[(CHC_5H_8CH)_xCH^tBu](NAr)[OCMe_2(CF_3]_2$ reacts with double bonds in the growing chain.

$W(CH^tBu)(NAr)(O^tBu)_2$,[17] on the other hand, *does not react* with *cis*-2-pentene appreciably in 24 h. Yet it reacts readily with norbornene to give $W[(CHC_5H_8CH)_xCH^tBu](NAr)(O^tBu)_2$.[18] At 25 °C virtually all of the initial neopentylidene complex is consumed by ~10 equiv of norbornene (Figure 1). It is important to note that the cis content of this living oligomer changes only very slowly with time (~10% in 24 h),[18] consistent with low activity of this catalyst toward ordinary double bonds. Addition of ~3 equiv of benzaldehyde to the living oligomer results in a rapid Wittig-like reaction as shown in eq 1 (P indicates polymer).[19] Figure 2 shows resonances that we ascribe to the oxo complex $W(O)(NAr)(O^tBu)_2$ and PhCH=CHP ($\gtrsim$90% trans about the PhCH=C bond) along with excess benzaldehyde.

$$W(CHP)(NAr)(O^tBu)_2 + PhCHO \rightarrow W(O)(NAr)(O^tBu)_2 + trans\text{-}PhCH{=}CHP \quad (1)$$

The addition of 50–200 equiv of norbornene to $W(CH^tBu)(NAr)(O^tBu)_2$ in toluene at 25 °C followed by addition of benzaldehyde yields benzylidene/neopentylidene-capped polynorbornene. The molecular weight of the major fraction corresponds approximately to the number of monomers added, and the polydispersity is approximately 1.05 (Table I). A typical GPC trace is shown in Figure 3. The variable amount (10–20%) of high molecular weight polymer that is formed we believe is due to a trace (≈1% of the catalyst) of an extremely active, as yet unidentified, tungsten–carbene species present during the polymerization.[23]

The production of monodispersed polymer that does not degrade, as shown by the lack of isomerization to the trans isomer after long reaction periods, requires that the polymer be "living." The degree of control that can be exercised by varying the nature of the alkoxide ligands in complexes of the type $W(CHR)(NAr)(OR')_2$ that we have outlined here should allow the preparation of polymers made from other strained monomers and block copolymers. Further studies are in progress.

Table I
Polynorbornene Formed by Employing $W(CH^tBu)(NAr)(O^tBu)_2$ as the Catalyst Followed by Quenching with Benzaldehyde[a]

equiv NBE	M_n (unc)	polydispersity	M_n (th)	M_n(unc)/ M_n(th)
50	10900	1.07	4700	2.3
100	23900	1.05	9400	2.6
200	46200	1.03	18800	2.5

[a] The polynorbornene sample was prepared by adding a solution of NBE in toluene (30 mL) dropwise at 25 °C to a rapidly stirred solution of 20 mg of catalyst in 5 mL of toluene under a nitrogen atmosphere. The reaction was quenched by addition of 10 μL of benzaldehyde. After 10 min the solvent was removed in vacuo and the polymer congealed by addition of methanol. The polymer was analyzed on a Waters 150C instrument in toluene at 25 °C vs. polystyrene standards. [b] Katz[24] has suggested that M_n (uncorrected vs. polystyrene) be divided by 2.0 to obtain the actual M_n for polynorbornene. These results suggest that a conversion factor of 2.2 may be more accurate.

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Registry No. $W(CH^tBu)(NAr)[OCMe(CF_3)_2]_2$, 101249-40-5; $W(CH^tBu)(NAr)[OCMe_2(CF_3)]_2$, 107440-83-5; $W(CH^tBu)(NAr)(O^tBu)_2$, 107440-84-6; polynorbornene, 25038-76-0.

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(13) In a typical experiment with [W] = 0.012 M and [norbornene] = 0.63 M, the rate was 18 equiv/h.
(14) The following signals appeared, each of approximately equal intensity (30% integration of one proton of original catalyst): δ 6.72 (t, J = 7 Hz), 6.26 (t, J = 8 Hz), 4.73 (m), 4.23 (m), 3.67 (m), 0.55 (t, J = 8 Hz), 0.28 (t, J = 8 Hz), −0.02 (br s). Other peaks may be obscured by polymer resonances. Upon use of 2,3-dideuterionorbornene only polymer olefinic signals were observable by ^2H NMR. The corresponding ^1H NMR was missing the signals at δ 6.26, 4.73, and −0.02.
(15) (a) $W(CH^tBu)(NAr)[OCMe_2(CF_3)]_2$ was prepared on a 1-mmol scale in ~40 mL of ether at −30 °C by adding $LiOCMe_2(CF_3)$ to $W(CH^tBu)(NAr)(dme)Cl_2$.[6] Recrystallization of the crude product from a minimum amount of pentane at −30 °C yielded the pure product as slightly oily, yellow-orange crystals in 60%

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 $W(CH^tBu)(NAr)[OCMe_2(CF_3)]_2$ in 1.0 mL of C_6D_6. The solution was heated for 5.5 h at 45 °C. By ^1H NMR the ratio of $W(CHEt)(NAr)[OCMe_2(CF_3)]_2$ to $W(CH^tBu)(NAr)[OCMe_2(CF_3)]_2$ 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) $W(CH^tBu)(NAr)(O^tBu)_2$ was prepared by adding 407 mg of LiO^tBu (5.08 mmol) to 1.50 g of $W(CH^tBu)(NAr)(dme)Cl_2$[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 $W(CH^tBu)(NAr)(O^tBu)_2$ 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 $W(CH^tBu)(NAr)(O^tBu)_2$ (20 mg) in 500 μL of toluene-d_8. An ^1H 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 $Ta(CH^tBu)(CH_2{}^tBu)_3$[20] and titanium–methylene complexes.[21] Recently, five coordinate tungsten alkylidene complexes have been reported to behave similarly.[22] What we believe to be $W(O)(NAr)(O^tBu)_2$ and largely *trans*-$^tBuCH{=}CHPh$ are formed upon reaction of $W(CH^tBu)(NAr)(O^tBu)_2$ with benzaldehyde. $W(O)(NAr)(O^tBu)_2$ 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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(23) We thought it possible that traces of water might produce the unknown very active catalyst. However, addition of 0.01–0.10 equiv/W of water to the $OCMe(CF_3)_2$ catalyst system gave *lower* molecular fractions. This phenemenon is still being investigated.

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R. R. Schrock,*[1] J. Feldman,[1] L. F. Cannizzo,[2] and R. H. Grubbs*[2]

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
and the Arnold and Mabel Beckman
Laboratories of Chemical Synthesis
Division of Chemistry and Chemical Engineering
California Institute of Technology
Pasadena, California, 91125

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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]

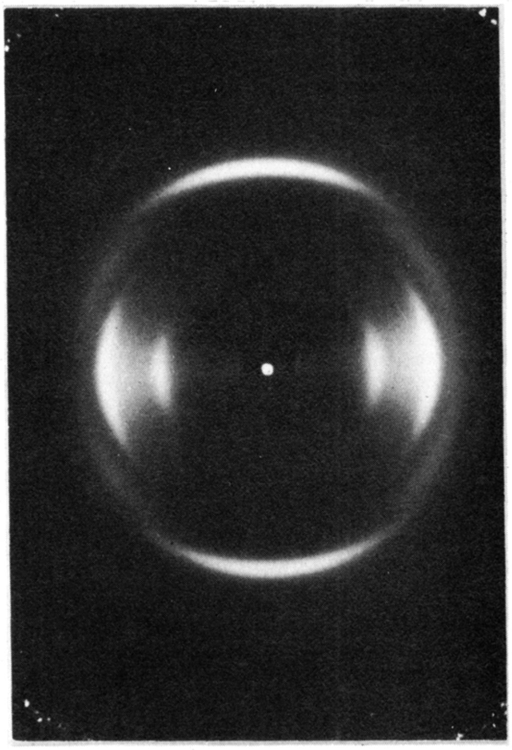

Figure 1. X-ray diffraction pattern of the poly[(1→4)-α-D-galactosamine] fiber annealed in water at 140 °C. Fiber axis is vertical.

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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