Polymerization of Bicyclic Acetals. 6. Synthesis and Polymerization of (+)-(1*R*,5*S*)-6,8-Dioxabicyclo[3.2.1]octane[1]

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ABSTRACT: An optically active, stereoregular polyacetal possessing a backbone structure similar to that of natural dextran but opposite absolute configurations of the asymmetric carbons was newly prepared by the cationic polymerization of (+)-(1*R*,5*S*)-6,8-dioxabicyclo[3.2.1]octane (**1***). The optically active monomer **1*** was synthesized from sodium 3,4-dihydro-2*H*-pyran-2-carboxylate (**2**) through the optical resolution of its diastereomeric dehydroabietylammonium carboxylate (**4**). Ring-opening polymerization of **1*** was carried out in methylene chloride at −93, −78, and −30 °C by using boron trifluoride etherate as an initiator. ^{1}H- and ^{13}C-NMR analysis of the resulting polymers revealed that highly stereoregular polymers were formed at −93 and −78 °C. The polymer obtained at −93 °C had a number average molecular weight of 6.8×10^4, melting at 172–175 °C and showing a specific rotation of $[\alpha]^{33}_D$ −198° (chloroform).

Synthetic saccharides and their derivatives from noncarbohydrate sources are of particular interest for the understanding of the elaborate functions characteristic of naturally occurring carbohydrates. Most of the works so far reported in this field have dealt with racemic compounds,[2] and there have been only few examples for the synthesis of optically active carbohydrates.[3] Recently attention has been directed by several groups of investigators toward chemical synthesis of polysaccharide analogues by ring-opening polymerization of bicyclic acetals.[1,4–11] For instance, cationic polymerization of 6,8-dioxabicyclo[3.2.1]octane has been shown to proceed at low temperature to yield a stereoregular high molecular weight polymer with a similar backbone to that of dextran consisting of α-D-glucose units linked predominantly in (1→6) fashion.[4,5] Furthermore, polysaccharide-type polymers having two hydroxyl groups per repeating unit have been successfully prepared by the chemical modifications of a stereoregular unsaturated polyacetal derived from 6,8-dioxabicyclo[3.2.1]oct-3-ene.[12,13] All of these polysaccharide analogues obtained by chemical reactions from noncarbohydrate materials were racemic, and it was desirable to synthesize optically active polymers, not only to clarify the microstructures of the corresponding racemic polymers but also to know the effect of stereoregularity on the properties and functions displayed by these polymers. As a first step toward this approach, polymerization of optically active 6,8-dioxabicyclo[3.2.1]octane was undertaken.

The present paper describes a convenient synthetic procedure for (+)-(1*R*,5*S*)-6,8-dioxabicyclo[3.2.1]octane (**1***) (1,6-anhydro-2,3,4-trideoxy-β-L-glycerohexopyranose in the nomenclature of carbohydrate chemistry) and its cationic polymerization leading to a polysaccharide analogue of the L series.

Experimental Section

Dehydroabietylamine. Dehydroabietylamine was purified by recrystallization of its acetate:[14] To a solution of 217 g of commercial dehydroabietylamine dissolved in 350 mL of toluene was added a solution of 43 g of acetic acid in 50 mL of toluene with ice cooling. The reaction mixture was stirred for a while to give white precipitates. After standing for about an hour at room temperature, the precipitates were collected and recrystallized three times from toluene to provide dehydroabietylammonium acetate (130 g): mp 106–112 °C; $[\alpha]^{26}_D$ +30.4° (ethanol, *c* 1.38) (lit.[14] mp 141–143.5 °C, $[\alpha]_D$ +30.2°).

Dehydroabietylammonium acetate (115 g) was dissolved in 200 mL of water by heating. To this solution 15 g of sodium hydroxide in 100 mL of water was added. After cooling the solution, the liberated dehydroabietylamine was extracted twice with 100 mL of ethyl ether. The combined ether extract was dried with anhydrous magnesium sulfate. The solvent was removed under reduced pressure to afford dehydroabietylamine as a light yellow oily residue.

Dehydroabietylammonium 3,4-Dihydro-2*H*-pyran-2-carboxylate. Sodium 3,4-dihydro-2*H*-pyran-2-carboxylate (50 g) was slightly acidified with 6*N* hydrochloric acid, and the resulting free carboxylic acid was extracted with 100 mL of ethyl ether twice. The ethyl ether extracts were combined and the solvent was removed as quickly as possible under reduced pressure. The residue was then added to an ice-cooled ether solution of dehydroabietylamine obtained from 109 g of dehydroabietylammonium acetate. After a recrystallization from methanol, crude crystals of dehydroabietylammonium 3,4-dihydro-2*H*-pyran-2-carboxylate were obtained in a yield of 47%.

The crude crystals (245 g) were recrystallized from methanol at least four times to give 100 g of white needles: mp 173–177 °C; $[\alpha]^{26}_D$ +10.7° (ethanol, *c* 1.05).

Ethyl 3,4-Dihydro-2*H*-pyran-2-carboxylate. The purified crystals of dehydroabietylammonium 3,4-dihydro-2*H*-pyran-2-carboxylate (99 g) were added to a solution of 11.5 g of sodium hydroxide in 200 mL of water with external cooling. To this solution, 100 mL of ethyl ether was added, and the heterogeneous mixture was shaken violently. When all the crystals were dissolved, the two layers were separated. The aqueous layer, having been extracted with ethyl ether, was evaporated under reduced pressure with a rotary evaporator below 50 °C. A white residue was dried under vacuum and then pulverized. The white powder was subsequently placed in a three-necked flask, to which 100 mL of dimethylformamide was added. The reaction mixture was heated at 75–80 °C with vigorous mechanical stirring, to which 68 g of ethyl iodide was added through a dropping funnel. After the addition of ethyl iodide, the reaction mixture was further heated for about 2 h. Then the reaction mixture was cooled to room temperature, 100 mL of water was added, and the resulting solution was extracted with 100 mL of benzene. The benzene extract was washed with 100 mL of water twice and dried with anhydrous sodium sulfate. The benzene was removed by fractional distillation, and the residue was distilled under reduced pressure to give ethyl 3,4-dihydro-2*H*-pyran-2-carboxylate: yield, 25.5 g (68%); bp 57 °C (3 mmHg); $[\alpha]^{26}_D$ −69.3° (ethanol, *c* 1.53) (lit.[15] bp for racemic compound 84.0–84.2 °C (10 mmHg)).

2-Hydroxymethyl-3,4-dihydro-2*H*-pyran. Lithium aluminum hydride (6 g) was dissolved in 60 mL of dry ethyl ether. With circulating cold water through a condenser, 22 g of ethyl 3,4-dihydro-2*H*-pyran-2-carboxylate in 20 mL of ethyl ether was added dropwise over 1 h. Then 5 mL of water was added drop by drop to the reaction mixture with caution to avoid bumping. After the excess lithium aluminum hydride reacted completely, 30% aqueous Rochelle salt was added to the cement-like reaction mixture. The mixture turned into a solution. The ether layer was separated and the aqueous layer was extracted with 100 mL of ethyl ether repeatedly. The combined ether extract was dried over magnesium sulfate and filtered, and the filtrate was freed from the solvent by fractional distillation. The residue was

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distilled under reduced pressure to give 14 g (87%) of 2-hydroxymethyl-3,4-dihydro-2*H*-pyran: bp 101 °C (50 mmHg); $[\alpha]^{28}_{D}$ −31.2° (benzene, *c* 0.89) (lit.[16] bp for racemic compound 100–103 °C (47 mmHg)).

6,8-Dioxabicyclo[3.2.1]octane.[17,18] *p*-Toluenesulfonic acid (0.099 g) was added to 100 mL of dry benzene and was dissolved by refluxing for 1 h. After cooling, 11 g of 2-hydroxymethyl-3,4-dihydro-2*H*-pyran was added and the mixture was refluxed for 2 h. After cooling, an excess of sodium methoxide (1.1 g) was added to neutralize the acid and the reaction mixture was stirred at room temperature for 0.5 h. The precipitates were separated by filtration and benzene was removed by fractional distillation. The residue was distilled in an apparatus with a Liebig condenser through which warm water of about 50 °C was circulated to avoid solidification of the distillate during distillation: yield, 7.6 g (68%); bp 67 °C (42 mmHg); $[\alpha]^{29}_{D}$ +111.4° (*n*-hexane, *c* 0.75) (lit.[19] bp for racemic compound 64–66 °C (38 mmHg)).

Polymerization of 6,8-Dioxabicyclo[3.2.1]octane. The monomer 1* was dissolved in methylene chloride and the solution was stirred over calcium hydride for a few days followed by distillation under reduced pressure. Methylene chloride was refluxed over phosphorus pentoxide and distilled. Boron trifluoride etherate was distilled just before use. The monomer and solvent were charged in a glass ampule, and an initiator solution was added to the mixture chilled in liquid nitrogen. The ampule was evacuated, sealed off, and allowed to stand in a constant temperature bath. After the addition of a small amount of pyridine to terminate the polymerization, the reaction mixture was poured into a large volume of methanol to precipitate a methanol-insoluble polymer. A methanol-soluble polymer was recovered by concentrating the methanol solution under reduced pressure followed by pouring the residual solution into a mixed solvent of methanol and water (1:1 by volume). Both methanol-insoluble and -soluble polymers were purified by repeated reprecipitation from their methylene chloride solutions into methanol and methanol–water, respectively. The methanol-soluble polymer was obtained as white powder by freeze–drying of its benzene solution.

Characterization. ^{1}H- and ^{13}C-NMR spectra were taken in deuteriochloroform at room temperature using tetramethylsilane as internal reference with a JNM-MH-100 spectrometer working at 100 MHz and a JNM-FX-100 Fourier transform spectrometer working at 25 MHz, respectively.

Number average molecular weight of the methanol soluble polymers was determined with a Hewlett Packard vapor pressure osmometer Model 302 in benzene solutions at 37 °C. Molecular weight of the methanol-insoluble polymers was determined by gel permeation chromatography in chloroform at room temperature with a JASCO TRIROTOR using a calibration curve for the racemic polymer of 6,8-dioxabicyclo[3.2.1]octane.

Optical rotation was measured in various solvents with a JASCO Model DIP-4 instrument.

Results and Discussion

Preparation of (−)-(1*S*,5*R*)-6,8-dioxabicyclo[3.2.1]octane from D-glucose has been reported by Pecka and Černý.[20] This synthetic route, however, involves many steps and the overall yield is less than 2%. Therefore, other more efficient routes are desirable which may afford one of the enantiomers of 6,8-dioxabicyclo[3.2.1]octane, preferably (+)-enantiomer, in a higher yield. The synthetic route adopted here uses sodium 3,4-dihydro-2*H*-pyran-2-carboxylate (2) as a starting material and involves the optical resolution of the diastereomeric salt (4) of optically active dehydroabietylamine (3), a base which has recently been used as a resolving reagent in the optical resolution of some carboxylic acids[14,21] (Scheme I).

Sodium 3,4-dihydro-2*H*-pyran-2-carboxylate (2) was converted with hydrochloric acid to its free carboxylic acid, which reacted readily with 3 to provide diastereomeric dehydroabietylammonium 3,4-dihydro-2*H*-pyran-2-carboxylate (4) as white needles. Repeated recrystallization of 4 from methanol solution afforded white crystals having a constant specific rotation of 10.7° in ethanol. The ammonium salt thus purified was then treated with aqueous sodium hydroxide to yield optically active sodium 3,4-dihydro-2*H*-pyran-2-carboxylate (2*). It was esterified with ethyl iodide in benzene, and the resulting ethyl ester (5*) was subsequently reduced with lithium aluminum hydride in dry ethyl ether to the corresponding alcohol (6*). It was cyclized in benzene containing a catalytic amount of *p*-toluenesulfonic acid to give the final product, optically active 6,8-dioxabicyclo[3.2.1]octane (1*). The overall yield from the racemic sodium carboxylate 2 was 8.4%.

Scheme I
Synthetic Route of (+)-(1*R*,5*S*)-6,8-Dioxabicyclo[3.2.1]octane

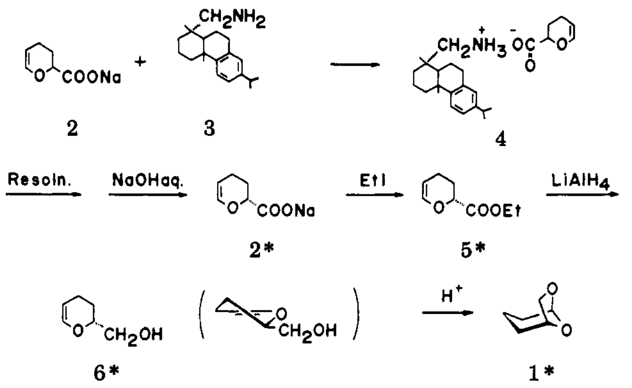


Table I
Polymerization of (+)-(1*R*,5*S*)-6,8-Dioxabicyclo[3.2.1]octane (1*) in Methylene Chloride[a]

expt no.	1*, g	temp, °C	MeOH insol polymer,[b] %	MeOH sol polymer,[c] %
PD*-10	0.56	−30	82	12
PD*-11	0.56	−78	84	trace
PD*-12	0.56	−93	75	trace

[a] CH_2Cl_2, 1.1 mL; BF_3OEt_2, 2 mol % to monomer; polymerization time, 2 h. [b] Methanol-insoluble polymer. [c] Methanol:water (1:1 vol ratio) insoluble polymer.

The optically active monomer 1* thus obtained showed a specific rotation of +111.4° in *n*-hexane. On the other hand, (−)-(1*S*,5*R*)-6,8-dioxabicyclo[3.2.1]octane derived from D-glucose was reported to show a specific rotation of −115° in *n*-hexane.[20] Considering its synthetic route, the latter monomer must have been 100% optically pure. Therefore, it follows from these values that the optical purity of the monomer 1* prepared in the present work is 97% and that the absolute configuration of the monomer 1* is, as we hoped, opposite to that obtained from D-glucose, namely, 1* is a so-called L-saccharide derivative. The ^{1}H- and ^{13}C-NMR spectra of 1* were the same as those of the racemic compound. DSC measurement disclosed that the optically active 1* had a melting point of 48.1–49.2 °C, which was about 1 °C lower than that of the racemic monomer.

Previous studies have shown that racemic 6,8-dioxabicyclo[3.2.1]octane undergoes cationic polymerization to yield a stereoregular high molecular weight polymer at low temperature.[4,5,8,9] The polymerization of the optically active monomer 1* was carried out in methylene chloride with boron trifluoride etherate as initiator at −30, −78, and −93 °C (Table I).

The ^{1}H-NMR spectra of the polymers obtained at −30 and −78 °C (PD*-10 and PD*-11) are shown in Figures 1 and 2, respectively. The ^{1}H-NMR spectra of the polymers obtained at −78 and −93 °C (PD*-11 and PD*-12) were

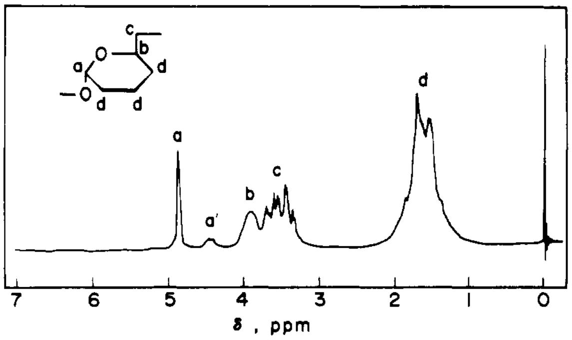


Figure 1. ^{1}H-NMR spectrum of the methanol-insoluble part of optically active poly(tetrahydropyran-2,6-diyloxymethylene) prepared at -30 °C (PD* -10): solvent, $CDCl_3$; concentration, 4%; 100 MHz.

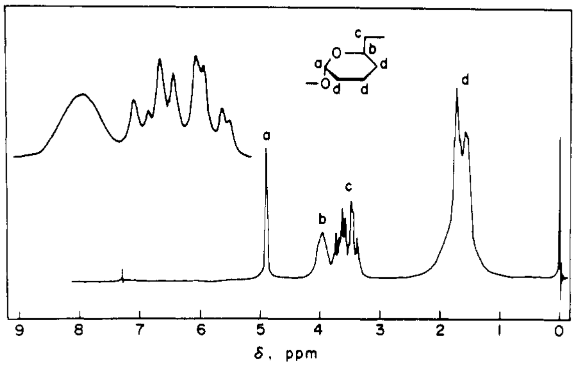


Figure 2. ^{1}H-NMR spectrum of optically active poly(tetrahydropyran-2,6-diyloxymethylene) prepared at −78 °C (PD* −11): solvent, $CDCl_3$; concentration, 5%; 100 MHz.

completely identical. There was no difference between the ^{1}H-NMR spectra of the methanol-insoluble and -soluble fractions of the polymer obtained at −30 °C (PD*-10) indicating that fractionation occurred depending on the molecular weight, not on the stereoregularity. The ^{1}H-NMR spectra of the optically active polymers are essentially the same as those of the racemic polymers obtained under similar conditions. The signal at δ 4.46 appearing only in the spectrum of the polymer obtained at −30 °C is ascribable to the axial acetal proton of the tetrahydropyran ring, that is, it shows the presence of the structural unit of "β form" in the terminology of carbohydrate chemistry. On the contrary, the polymers prepared at lower temperatures exhibit only equatorial acetal proton signal at δ 4.88, which demonstrates that these polymers entirely consist of "α form".

The oxymethylene proton signals of the optically active polymers obtained at −78 and −93 °C showed an ABX pattern in the region of δ 3.28–3.80 as shown in the expanded spectrum in Figure 2. The analysis of the pattern gave the estimated values of the coupling constants, $J_{AB} = 10.6$ Hz, $J_{AX} = 5.9$ Hz, and $J_{BX} = 3.7$ Hz. The latter two values indicate that the conformation around the exocyclic C–C bond is not fixed at one of the three noneclipsing conformations.

The ^{13}C-NMR spectra of the polymers obtained at −30 and −78 °C (PD*-10 and PD*-11) are shown in Figures 3 and 4, respectively. The fact that the latter spectrum consists of only six signals indicates clearly that the polymer prepared at lower temperature is highly stereoregular. On the contrary, in the former spectrum, there were seven additional signals which undoubtedly arise from the presence of the "β form" along the polymer chain. These signals were assigned on the basis of the off-resonance spectrum and the comparison of the observed chemical shifts with those reported for naturally occurring (1→6) disaccharides, isomaltose, and gentiobiose.[22] The ^{13}C-NMR chemical shifts and their assignments are summarized in Table II and the accompanied structural formulas. The data for a racemic polymer are also included in Table II for comparison.

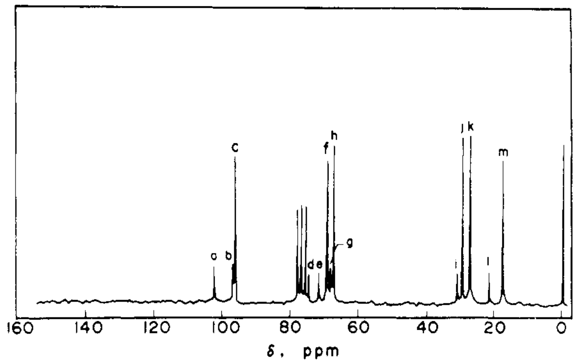


Figure 3. ^{13}C-NMR spectrum of the methanol-insoluble part of optically active poly(tetrahydropyran-2,6-diyloxymethylene) prepared at −30 °C (PD* −10): solvent, $CDCl_3$; concentration, 4%; 2000 scans; 25 MHz.

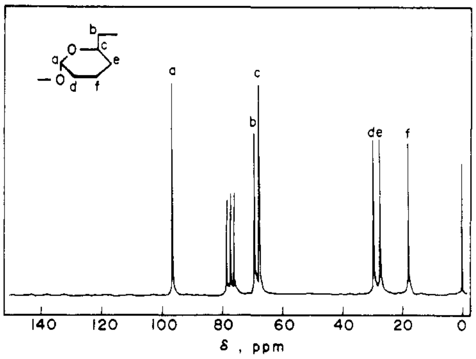


Figure 4. ^{13}C-NMR spectrum of optically active poly(tetrahydropyran-2,6-diyloxymethylene) prepared at −78 °C (PD* −11): solvent, $CDCl_3$; concentration, 5%; 5000 scans; 25 MHz.

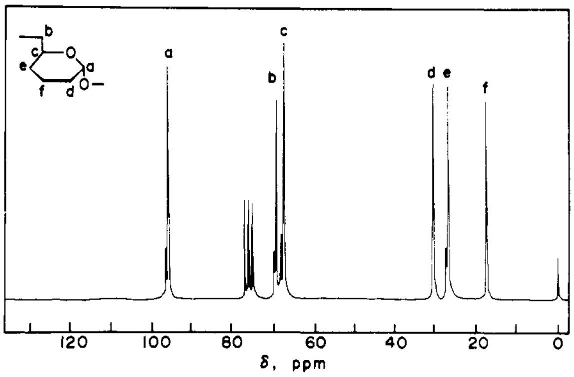
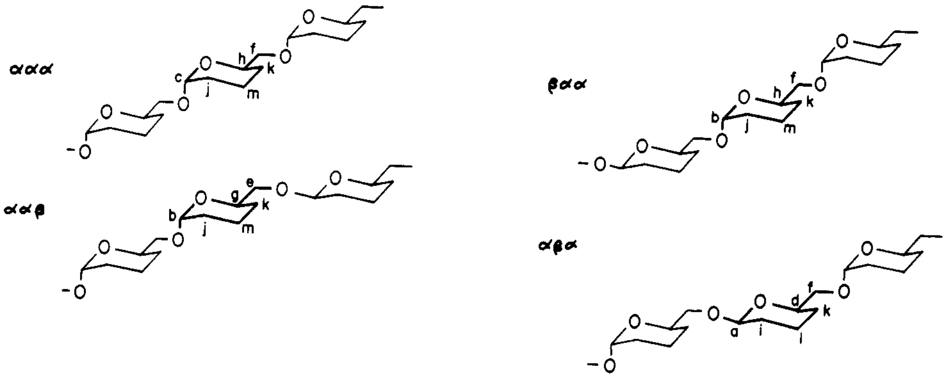


Figure 5. ^{13}C-NMR spectrum of racemic poly(tetrahydropyran-2,6-diyloxymethylene) prepared at −78 °C: solvent, $CDCl_3$; concentration, 10%; 25 MHz.

Figure 5 gives the ^{13}C-NNR spectrum of the racemic polymer prepared in methylene chloride at −78 °C with boron trifluoride etherate as initiator. It is noteworthy that the signals a, b, c, and e consist of a pair of peaks of different intensities and that the chemical shift of the higher field peak of each pair is in complete agreement with that of the corresponding peak for the optically active polymer (Table II). In view of the fact that the racemic polymer does not contain any structural unit of the "β form", the lower field peak of each signal pair can be reasonably ascribed to dyad structures consisting of D–L enantiomer pair. The area ratio of the higher field peak

Table II
Chemical Shifts and Assignments of ^{13}C-NMR Spectra of Optically Active and Racemic Poly(tetrahydropyran-2,6-diyloxymethylene)'s[a]



assignment[b]	a	b	c	d	e	f	g	h	i	j	k	l	m
PD*-10	102.63	97.27	96.63	74.75	71.83	69.24	68.32	67.49	31.14	29.58	27.48	21.83	17.93
PD*-11			96.49			69.10		67.39		29.43	27.34		17.93
PD*-12			96.49			69.05		67.40		29.43	27.34		17.88
racemic[c]			97.27 96.49			69.68 69.05		68.13 67.39		29.43	27.87 27.34		17.88

[a] Spectra were measured in $CDCl_3$ at room temperature. Chemical shift values are given in ppm from tetramethylsilane.
[b] The assignments a through m for PD*-10 correspond to the peaks a through m in Figure 3. The assignments c, f, h, j, k, and m for PD*-11, PD*-12, and racemic correspond to the peaks a, b, c, d, e, and f, respectively, in Figures 4 and 5.
[c] Racemic polymer prepared at −78 °C in CH_2Cl_2.

Table III
Characterization of Optically Active Poly(tetrahydropyran-2,6-diyloxymethylene)

polymer	α-form content,[a] %		M_n[b] × 10^{-3}	mp, °C	$[\alpha]_D$ in $CHCl_3$	
	^{1}H	^{13}H			deg	c[c]
PD*-10[d]	82	80	1.5[e]	61-64		
PD*-10[f]	85	83	12	95-99	−136	0.98
PD*-11	100	100	37	167-170	−195	0.84
PD*-12[g]	100	100	68	172-175	−198	0.71

[a] Determined from NMR spectrum. [b] By gel permeation chromatography in chloroform (column: Shodex 80M 1 m). [c] g/100 mL. [d] Methanol soluble fraction of PD*-10. [e] By vapor pressure osmometry in benzene at 37 °C. [f] Methanol-insoluble fraction of PD*-10. [g] Elementary Anal. Calcd for $(C_6H_{10}O_2)_n$: C, 63.18; H, 8.77. Found: C, 63.24; H, 8.90.

to the lower field peak of each signal pair is approximately 4:1, which demonstrates that the racemic polymer prepared under the conditions described above is rich in isotactic dyad. Further details on the stereoregularity of the racemic polymers will be described in a forthcoming publication.

Some characterization data of the optically active polymers were summarized in Table III. The α-form content in the polymers was estimated independently from ^{1}H-NMR (100a/(a + a′)) and ^{13}C-NMR spectra (100c/(a + b + c)) by using the relative intensities of the acetal proton and carbon signals, respectively. The α-form contents determined in these two ways were in good agreement with each other. The specific rotation of the polymer obtained at −30 °C (PD* −10) containing an appreciable amount of the structural unit of the "β form", as was expected, was of a smaller value than those for the polymers obtained at −78 and −93 °C (PD* −11 and PD* −12) entirely consisting of the structural unit of the "α form".

The X-ray diffraction pattern of the polymer obtained at −93 °C (PD* −12) showed crystalline peaks at $2\theta = 12.3$ and 18.5°, while that of the racemic polymer at $2\theta = 10.2$ and 18.0°. In view of the fact that the racemic polymer is essentially isotactic, this difference means that the racemic and optically active polymers have apparently different crystalline properties suggesting that the former polymer may crystallize with unit cells containing both *R* and *S* blocks.

The optically active polymer newly prepared in this work possesses a backbone structure similar to that of naturally occurring dextran but is completely opposite in the absolute configuration of the asymmetric carbons. Therefore, this polymer seems to be useful as a model compound for elucidating biological activities of natural polysaccharides. Furthermore, synthetic polysaccharides of the L series having two hydroxyl groups per repeating unit would be obtained by applying the synthetic procedure for the optically active bicyclic acetal **1*** to the preparation of its unsaturated analogues, and by following the synthetic routes for the racemic hydroxylated polymers already developed by the authors.[12,13]

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Polymerization of Phenylacetylenes. 8. Simultaneous Coordination and Cationic Polymerizations in the WCl_6-Catalyzed Copolymerization of Phenylacetylene with Styrene

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ABSTRACT: The WCl_6-catalyzed copolymerization of phenylacetylene with styrene was investigated. Chromatographic and spectroscopic analyses showed that the product was a mixture of poly(phenylacetylene) and a copolymer of styrene with phenylacetylene. The effects of solvent, reducing agent, and catalyst on the copolymerization were studied. It was concluded that poly(phenylacetylene) was produced by coordination polymerization and the copolymer of styrene with phenylacetylene was formed by cationic polymerization simultaneously in a homogeneous system. Either the coordination or cationic polymerization could selectively be brought about by choosing suitable reaction conditions.

In a previous paper it was reported that WCl_6 and $MoCl_5$ worked as effective catalysts for the polymerization of phenylacetylene.[1] The effects of solvent,[1] substituent,[2] reducing agent,[3] and chain transfer agent[4] were examined in detail for this polymerization. The results obtained showed that the WCl_6-catalyzed polymerization of phenylacetylene proceeded by a coordination mechanism. The polymerization behavior resembled in several aspects that of cycloolefin polymerization by tungsten-based catalysts. On the other hand, WCl_6 has been known as a Lewis acid. For example, it can catalyze the cationic polymerization of styrene[5] and 2,4-hexadiene,[6] as most metal halides do.

Thus, WCl_6 can catalyze two totally different kinds of polymerizations, that is, coordination or cationic polymerization depending on the kind of monomer present. It seems, therefore, of great interest to study the WCl_6-catalyzed copolymerization of phenylacetylene with styrene, associated with the following questions: What is the copolymerization product and what mechanism is governing this copolymerization?

This paper deals with monomer reactivities, products, and reaction mechanisms in the WCl_6-catalyzed copolymerization of phenylacetylene with styrene.

Experimental Section

Materials. Phenylacetylene was prepared by the bromination of styrene and the subsequent dehydrobromination. Tungsten hexachloride was commercially obtained (Mitsuwa Chem. Corp., purity >99%) and used without further purification. Styrene and other reagents for polymerization were purified by the usual methods. Spectroscopic grade reagents were used for measuring UV–vis and fluorescence spectra.

Polymerization. The polymerizations of phenylacetylene and styrene were carried out in a 30-mL Erlenmeyer flask equipped with a three-way stopcock under a dry nitrogen atmosphere. Unless otherwise stated, polymerization was performed at 30 °C with a catalyst concentration of 10 mM and a total monomer concentration of 1.0 M.

Water, half as much as WCl_6, was added to the WCl_6 catalyst; the catalyst system is denoted as $WCl_6 \cdot {}^1/_2H_2O$. This amount of water enhances polymer yield yet hardly affects polymer molecular weight or polymer structure.[1] The $WCl_6 \cdot Ph_4Sn$ catalyst was prepared by mixing equimolar amounts of WCl_6 and tetraphenyltin in a solvent and by aging for 15 min at 30 °C before use. The $SnCl_4 \cdot CCl_3CO_2H$ catalyst is an equimolar mixture of $SnCl_4$ and CCl_3CO_2H in a solvent.

The conversion of each monomer was monitored by measuring the amount of residual monomer by gas chromatography in aliquots taken at given intervals. Polymer samples were isolated by pouring the reaction products into a large amount of methanol. When necessary, the products were washed with a mixture of methanol and concentrated hydrochloric acid (9:1 volume ratio) to remove the catalyst residue.

Polymer Characterization. The number-average molecular weight of polymers was determined by vapor pressure osmometry using a Hitachi 117 osmometer.

Thin-layer chromatography was performed as follows: A silica gel plate (E. Merck 60 F_{254}; layer thickness 0.25 mm) was used as a stationary phase. Immediately before use, ether was used for purification and the gel layer was activated for 1 h at 120 °C. Stock solutions were prepared by use of carbon tetrachloride as a solvent (2.0 g/dL for No. 1 and 3 and 5.0 g/dL for No. 2 and 4; see Table I for the numbers). A spot of each solution, containing 40 μg or 200 μg of polymers for No. 1 and 3 and Nos. 2 and 4, respectively, was formed on the gel layer. A mixture of carbon tetrachloride and benzene (50:50 volume ratio) was used as a developer. After developing, the positions of the polymers were visualized by exposing the plate to iodine vapor.

The gel permeation chromatograms of polymers were recorded on a Toyo Soda HLC801A (column: GMH, 4 ft) using tetrahydrofuran as a solvent (0.30 w/v %).

UV–vis spectra were observed in ethylene dichloride (concentration 2.0×10^{-4} M) on a Shimadzu UV210 spectrophotometer.

Fluorescence spectra were observed in tetrahydrofuran (concentration 5.0×10^{-5} M) using a Hitachi MPF4 fluorescence spectrophotometer. Emission spectra were measured by exciting at 270 nm (excitation band width 4 nm; emission band width 10 nm). The emission intensity was well corrected against wavelength dependence.

Differential thermal analysis was performed on a Shimadzu DT-20B analyzer. All runs were made at a heating rate of 10 °C/min in a temperature range of 30–270 °C under a helium stream (30 mL/min) with α-alumina as the reference. Temperature was corrected by measuring the melting point of indium (156.4 °C).

Results and Discussion

Copolymerization of Phenylacetylene with Styrene under Various Conditions. Figure 1 shows the time–

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