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where we include lowest order corrections in $\delta = (\pi/3)(b_p/R_0)[l_m/(2|\ln \rho(\infty))|]^{1/2}$. Estimating the experimentally controlled parameters, $T \simeq 0.5$, $l_m \simeq 10$, $\rho_m(0)/\rho_m(\infty) \simeq 300$, we find that the solutions converge rapidly (i.e., are close to $\rho_p(0)$ and $\rho_m(0)$) provided that the polymer volume fraction in the nucleus, $N_p/(4\pi/3)R_0{}^3\rho_p{}^*$, is much smaller than 0.15 ($\rho_p{}^*$ is the close-packed polymer density). Corrections lead to a slight increase of size of the critical droplet due to chain penetration into the droplet–vapor interface driven by entropy of confinement effects[6] (of order $(b_p/R_0)^2$).

We conclude this note by commenting on an interesting aspect of polymer growth in supersaturated vapor. In the absence of nucelation, low temperature and polymer concentration will lead to a collapsed (globular) state of the polymer chain.[6] However, once enough monomers are adsorbed on the polymer, the critical droplet size is reached and the droplet proceeds to grow to macroscopic dimensions. The polymer chain expands inside the droplet until the swollen configuration corresponding to a polymer in good solvent is reached. Thus, the nucleation process is accompanied by the globule-to-coil transition of the polymer.

Acknowledgment. Although the information in this document has been funded by the U.S. Environmental Protection Agency under assistance agreement CR 807864-02-0 to the National Center for Intermedia Transport Research, it does not necessarily reflect the views of the Agency, and no official endorsement should be inferred.

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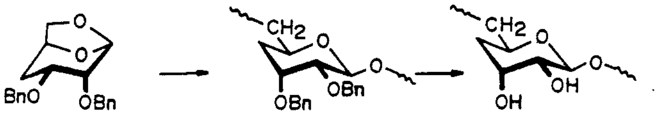
Communications to the Editor

Chemical Synthesis of Polysaccharides. 4. 4-Deoxy-(1→6)-β-DL-*ribo*-hexopyranan, the First Example of a (1→6)-β-Linked Polysaccharide Synthesized by the Ring-Opening Polymerization Method

In recent years, a variety of polysaccharides and their analogues have been synthesized by the cationic ring-opening polymerization of anhydrosugar derivatives.[1-6] Above all, the polymerization of 1,6-anhydrosugar derivatives has been most extensively investigated, since it often yields high molecular weight stereoregular polymers exclusively composed of (1→6)-α-pyranosyl residues under appropriate reaction conditions, particularly at low temperatures. With the rise in polymerization temperature, the stereoregularity of the polymers is generally lost because of the concomitant formation of (1→6)-β-pyranosyl residues along with the predominant (1→6)-α-pyranosyl residues.[7] To the best of our knowledge, there has been no publication dealing with the chemical synthesis of polysaccharides predominantly or exclusively consisting of (1→6)-β-pyranosyl residues from 1,6-anhydrosugar derivatives. In the present communication, we report the chemical synthesis of 4-deoxy-(1→6)-β-DL-*ribo*-hexopyranan (**3**) by the ring-opening polymerization of a bicyclic acetal (**1**) derived from noncarbohyrates sources, followed by debenzylation of the resulting polymer (**2**).[8] This is the first example of a regularly (1→6)-β-linked polysaccharide obtained by the ring-opening polymerization method.



1 Bn, $-CH_2C_6H_5$ 2 3

Monomer **1**, 3(e),4(a)-bis(benzyloxy)-6,8-dioxabicyclo[3.2.1]octane (1,6-anhydro-2,3-di-*O*-benzyl-4-deoxy-β-DL-*ribo*-hexopyranose), was synthesized from 3,4-dihydro-2*H*-pyran-2-carbaldehyde (acrolein dimer) via five reaction steps: The precursor of **1**, 3(e),4(a)-dihydroxy-6,8-dioxabicyclo[3.2.1]octane, was prepared by the procedures described by Brown et al.[9-11] with some modifications. Subsequent benzylation of the dihydroxy compound by the conventional method using sodium hydride and benzyl chloride in dimethyl sulfoxide gave monomer **1** as white crystals. The monomer was purified by recrystallization three times from ethanol and finally from a mixture of *n*-hexane and dichloromethane (2.5:1 volume ratio): mp 42.5–43.5 °C; ^{13}C NMR ($CDCl_3$, 50 MHz, Me_4Si) δ 138.34 and 138.17 (phenyl (ipso)), 128.18 (phenyl (meta)), 127.73 (phenyl (para)), 127.39 and 127.19 (phenyl (ortho)), 100.51 (C(5)), 73.74 (C(3)), 72.91 (benzyl), 71.94 (C(4)), 71.10 (C(1)), 70.31 (benzyl), 66.81 (C(7)), 32.47 (C(2)) (the numbering is based on the IUPAC nomenclature of organic chemistry). Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.71; H, 6.80.

Polymerization of **1** was carried out in three different solvents, toluene, dichloromethane, and 1-nitropropane, with phosphorus pentafluoride as initiator at −60 °C. A high-vacuum technique was employed for the polymerization. A polymer was separated from the reaction mixture by repeated reprecipitation using dichloromethane and methanol as a solvent–precipitant pair, followed by freeze-drying from a benzene solution. The results of the polymerization are presented in Table I.

The polymer prepared in toluene showed a higher melting point (Table I) and lower solubility than the polymers obtained in the other two solvents: The former polymer was soluble in benzene, chloroform, dichloromethane, 1,2-dimethoxyethane, and pyridine and insoluble in 1,4-dioxane, dimethylformamide, 1-nitropropane, and toluene, whereas the latter polymers were soluble in all these solvents. Such remarkable differences conceivably

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Table I
Polymerization of 3(e),4(a)-Bis(benzyloxy)-6,8-dioxabicyclo[3.2.1]octane (1)[a]

mmol of monomer	solvent	mL of solvent	time, min	yield, %	$M_n \times 10^{-4}$ [b]	mp, °C	β-form,[c] %
2.0	$C_6H_5CH_3$	3	50	25	2.3	120–156	~100
1.9	CH_2Cl_2	3	50	87	1.7	71–83	~100
2.0	1-$C_3H_7NO_2$	3	20	79	4.2	78–87	~100

[a] Initiator, PF_5, 0.10 mmol; temperature, −60 °C. [b] By gel permeation chromatography (polystyrene standard). [c] By ^{13}C NMR spectroscopy.

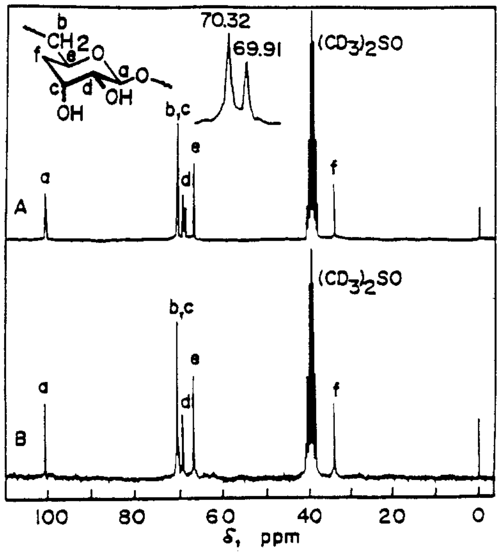

Figure 1. ^{13}C NMR spectra of 4-deoxy-(1→6)-β-DL-*ribo*-hexopyranan (3) (solvent, $(CD_3)_2SO$; temperature, 70 °C; 50 MHz; internal reference, Me_4Si): (A) Polysaccharide 3 derived from polymer 2 prepared in dichloromethane; (B) Polysaccharide 3 derived from polymer 2 prepared in toluene (Table I).

arise from the difference in the tacticity of the polymers as will be described later.

Debenzylation of polymer 2 was readily achieved with sodium in liquid ammonia to give a polysaccharide as a white fluffy powder after the conventional workup. Anal. Calcd for $(C_6H_{10}O_4)_n$: C, 49.31; H, 6.90. Found: C, 49.38; H, 7.01. Figure 1 shows the ^{13}C NMR spectra of the polysaccharides derived from the polymers 2 prepared in dichloromethane (A) and in toluene (B), respectively. The signals were assigned as indicated in the figure, their chemical shifts being δ 101.88 (a), 71.68 (b and c (overlapped)), 70.32 (d), 67.87 (e), and 35.30 (f) (solvent, $(CD_3)_2SO$; 70 °C; 50 MHz; internal reference, Me_4Si). The anomeric chemical shift of the polysaccharide corresponds to those for methyl β-D-gulopyranoside (δ 102.6[12]) and methyl β-D-allopyranoside (δ 101.9[13]).

It is noteworthy that signal d in spectrum A is split into two peaks of different intensities (δ 70.32 and 69.91), while every signal in spectrum B appears as singlets (signals b and c are overlapped). The polysaccharide derived from polymer 2 obtained in 1-nitropropane showed essentially the same ^{13}C NMR spectrum as spectrum A in Figure 1. When the ^{13}C NMR spectrum of the polysaccharide giving spectrum A in dimethyl-d_6 sulfoxide was measured in deuterium oxide, signals a and b as well as signal d were split into two peaks of different intensities, respectively. Particularly, the chemical shift difference between the split peaks of signal d became larger compared with that measured in dimethyl-d_6 sulfoxide: (a) δ 102.35, 102.00 (C(1)); (b) δ 73.06, 72.78 (C(6)); (c) δ 72.47 (C(3)); (d) δ 72.00, 71.30 (C(2)); (e) δ 68.96 (C(5)); (f) δ 34.81 (C(4)) (solvent, D_2O; 70 °C; 25 MHz; external reference, Me_4Si). Since monomer 1 is racemic, it seems reasonable to assume that such splittings of the signals are ascribable to the different dyad placements of the D,L-enantiomeric monomeric units in the polymer chains. In this connection, it is to be noted here that the polymers of racemic 6,8-dioxabicyclo[3.2.1]octane and its 4(e)-bromo derivative exhibited similar splittings of the signals in their ^{13}C NMR spectra and that these splittings were proved to arise from the dyad structures of the D–D and L–L consecutive units (isotactic dyad) and of the D–L enantiomer pair units (syndiotactic dyad) by comparison of their chemical shifts with those for the respective optically active polymers.[14–17] Therefore, the fact that every signal in spectrum B in Figure 1 appears as singlets clearly demonstrates that the stereoregularity of the polysaccharide derived from the polymer 2 obtained by polymerization in toluene is appreciably higher than the stereoregularity of the other two polysaccharides derived from the polymers 2 which were prepared in dichloromethane and in 1-nitropropane, respectively. Such a difference in the stereoregularity is reflected in the solubility of these polysaccharides; that is, the former polysaccharide is soluble only in dimethyl sulfoxide, whereas the latter polysaccharides are soluble in water as well.

The anomeric structure of pyranoses can always be determined from the one-bond coupling constant between the anomeric carbon and hydrogen, $J_{C\text{-}1,H\text{-}1}$.[13] For a number of methyl glycopyranosides, α-glycosides with an equatorial anomeric hydrogen give a $J_{C\text{-}1,H\text{-}1}$ value of 170 Hz, whereas β-glycosides with an axial anomeric hydrogen gave a $J_{C\text{-}1,H\text{-}1}$ value of 160 Hz.[18] This empirical rule is also valid for oligosaccharides and polysaccharides. For instance, (1→6)-α-D-linked dextran shows a $J_{C\text{-}1,H\text{-}1}$ value of 171 Hz, whereas (1→6)-β-D-linked pustulan shows a $J_{C\text{-}1,H\text{-}1}$ value of 160 Hz.[19,20] The polysaccharide synthesized in the present work gave a $J_{C\text{-}1,H\text{-}1}$ value of 160.2 Hz. The observed $J_{C\text{-}1,H\text{-}1}$ value together with the ^{13}C NMR chemical shift data leads us to the conclusion that the polysaccharide is entirely composed of (1→6)-β-linked pyranosyl residues; namely, it is 4-deoxy-(1→6)-β-DL-*ribo*-hexopyranan (3). This finding is in marked contrast to the general tendency that the ring-opening polymerization of 1,6-anhydrosugar derivatives at low temperatures affords polymers predominantly or exclusively consisting of (1→6)-α-linked pyranosyl residues. In other words, the polymerization of 1 proceeds by a mechanism different from an S_N2-type mechanism involving a propagating trialkyloxonium ion, which is commonly postulated for the ring-opening polymerization of 1,6-anhydrosugar derivatives giving rise to (1→6)-α-linked polymers.[2–6,21] It would appear that the equatorial and axial orientations of the vicinal bulky benzyloxy groups of monomer 1 play a decisive role in causing a dramatic change in the steric course of the propagation reaction. The mechanism for the unusual formation of the (1→6)-β-linked polymer and the significant solvent effect on the stereospecificity in the polymerization of monomer 1 are currently under investigation.

Registry No. 1, 92420-59-2; 2, 92420-58-1; 3, 92471-89-1; 3,4-dihydro-2*H*-pyran-2-carbaldehyde, 100-73-2; 3(e),4(a)-dihydroxy-6,8-dioxabicyclo[3.2.1]octane, 34339-25-8.

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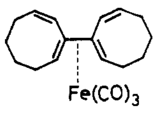
Novel Semiconducting Organometallic Polymers Containing $M(CO)_3(1,3\text{-diene})$ Groups (M = Fe, Ru)

The electrical properties of organometallic polymers containing mixed-valence transition metals have attracted much attention because of their unique conductivity behavior. $(Bis(fulvalene)diiron)^+(TCNQ)^{-\cdot}$ ($\sigma = 10^2$ S cm^{-1})[1] and the TCNQ salt of poly((3-vinylbis(fulvalene))diiron) ($\sigma = 10^{-3}$ S cm^{-1})[2] are among the best known examples. In our search for new semiconducting organometallic compounds, we have found that compressed disks of crystalline $Fe(CO)_3$[2-(1,7-cyclooctadienyl)-1,3-cyclooctadiene] (**1**)[3] prepared from $Fe_2(CO)_9$ and bis(2,4-cyclooctadienyl) show a fairly good conductivity ($\sigma_{dc} = 10^{-4}$ S cm^{-1}) at room temperature when doping was conducted with iodine. This finding prompted us to prepare novel conducting organometallic polymers containing a $M(CO)_3$(diene) group, which are readily cast into flexible films.



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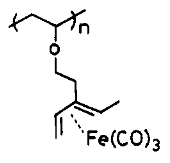

2(M=Fe), 3(M=Ru)

Table I
Direct-Current Conductivities for Undoped and Doped Organometallic Polymers

polymer	absorbed dopant/metal complex[a]	σ_{dc}, S cm^{-1}
polymer **2**	undoped	$<1.0 \times 10^{-10}$
polymer **2**	0.18 (I_2/Fe)	3.2×10^{-3}
polymer **2**	0.31 (SbF_6/Fe)	5.6×10^{-4}
polymer **3**	undoped	$<1.0 \times 10^{-10}$
polymer **3**	0.35 (I_2/Ru)	1.4×10^{-3}
polymer **6**	0.15 (I_2/Fe)	1.3×10^{-4}
copolymer(**6**/poly(MMA) = 1/1.2)	0.10 (I_2/Fe)	1.3×10^{-5}
copolymer(**6**/poly(MMA) = 1/5.8)	0.19 (I_2/Fe)	1.4×10^{-5}

[a] Molar ratio of absorbed dopant to metal complex.

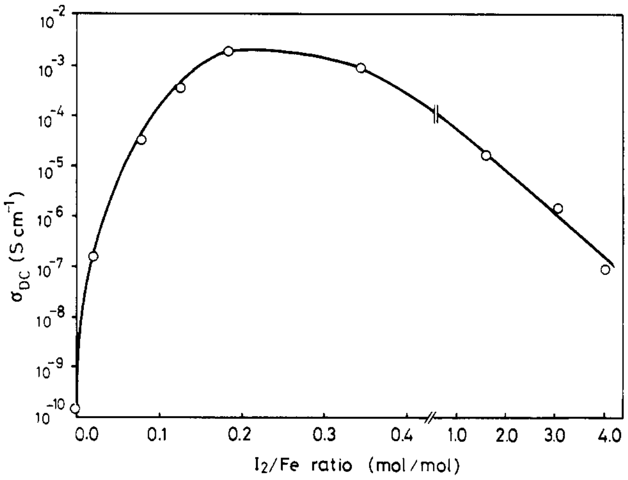

Figure 1. Dependence of dopant concentration (absorbed I_2) on the apparent conductivity of polymer **2**.

This paper describes the unique electrochemical properties of poly[$Fe(CO)_3$(3-((vinyloxy)ethyl)-η^4-1,3-pentadiene)] (**2**) and poly[$Ru(CO)_3$(3-((vinyloxy)ethyl)-η^4-1,3-pentadiene)] (**3**) after doping. Polymer **2** (M_n = 21 000) and polymer **3** (M_n = 15 000),[4,5] which are air-stable, can be cast into films by evaporation of their CH_2Cl_2 solutions and are insulators ($\sigma_{dc} < 10^{-10}$ S cm^{-1}). But doping with iodine increases the film conductivity by 6–7 orders of magnitude up to 3.2×10^{-3} S cm^{-1}, one of the highest values ever observed for organometallic polymers (Table I). When doping with iodine was conducted on films of **2** and **3** (thickness 0.1–0.15 mm) by sublimation, the direct-current conductivity increased rapidly in the range of I_2/Fe = 0.02–0.2 (mol/mol) to reach the level of $\sigma = 10^{-3}$ S cm^{-1} (Table I) before leveling off at I_2/Fe = 0.2 (Figure 1). The pale yellow film turned black on doping not only at the surface but also throughout the volume of the film. Addition of a large amount of dopant (I_2/Fe > 2.0) causes a decrease in conductivity. Doping with $(NO)SbF_6$ in nitromethane is also effective. Similar behavior has been observed in the doping of poly(vinylferrocene), poly(vinylferrocenylene), and poly(ethynylferrocene) with dichlorodicyanoquinone or iodine,[6] though their maximum conductivities (10^{-6}–10^{-9} S cm^{-1}) were 3–5 orders of magnitude lower than that of polymer **2**. Poly(ferrocenylmethyl methacrylate) (**4**) and poly(1-ferrocenylethyl methacrylate) (**5**), prepared by conventional methods,[7] also showed low conductivity (10^{-9} S cm^{-1}) after doping with iodine in the ratio I_2/Fe = 0.01–0.5. These results tell us that $[Cp_2Fe]^+I_3^-$ or its analogues[8] formed by doping do not construct semiconducting columns involving oriented $[Fe^{II}–Fe^{III}]^+$ species.

When polymer **2** doped with I_2 was held in a vacuum (10^{-2} torr for 1 day) or exposed to air (5 days), dedoping

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