# Preparation of High Molecular Weight 2,3,4-Tri-*O*-benzyl-[1→6]-α-D-gluco- and -galactopyranan and [1→6]-α-D-Glucopyranan

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ABSTRACT: In the polymerization of 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose, the acetyl fluoride–phosphorus pentafluoride complex is somewhat inferior to phosphorus pentafluoride alone as a catalyst. The acetyl fluoride apparently acts as a chain transfer agent. Traces of volatile hydroxylic solvents strongly adsorbed on monomer cause some catalyst deactivation. These can be removed by recrystallization from methylene chloride or petroleum ether. Smaller quantities of catalyst can then be used and higher molecular weight products obtained. Similar results are obtained with the corresponding galactose monomer. Osmotic pressure measurements establish that the $\overline{DP}_n$ values of the glucose derivatives reach as much as 900 and of the galactose derivatives nearly 500. Three or four chain breaks during debenzylation result in free polysaccharides of $\overline{DP}_n$ 100–250 (unfractionated). Viscosity–molecular weight relations are given.

The stereospecific polymerization of 1,6-anhydro sugar derivatives has been investigated in some detail[1-7] and has been shown to be a feasible method of synthesis of pure linear α-1,6′-linked polymers of glucose, mannose, and galactose and of comb-shaped oligomers and polymers.[8,9] Independent enzymic analyses[10-12] with exo and endo enzymes have indicated that the structures of both glucan and mannan are essentially completely α linked and contain only 1–3% structural flaws of any kind, and chemical evidence indicates the same degree of stereoregularity in the galactan as well.

In the following article we report some improvements in the preparation of 2,3,4-tri-*O*-benzyl-[1→6]-α-D-gluco- and -galactopyranan which identify the source of catalyst deactivation previously observed and which permit the formation of somewhat higher molecular weight polymers. We also report intrinsic viscosity–molecular weight relationships on these two polymers and report the molecular weights of several samples of unsubstituted glucan.

## Results and Discussion

In our first series of experiments, extreme precautions were taken to exclude impurities, by approximating the "living polymer" techniques[13] effective in anionic polymerization. A complex of phosphorus pentafluoride–acetyl fluoride (1:1)[14] was also employed as catalyst–cocatalyst combination in an attempt to simplify the initiation process. (See Experimental Section and Table I.)

Using these conditions with catalyst and cocatalyst, only 0.4 mol % was required to obtain 96% conversion (Table I, GL-5) of polymer equivalent in stereoregularity to our best [α] + 113.5 ± 0.3° (*c* 1, $CHCl_3$) (instead of a previous minimum of 2.5%). Nevertheless, the highest viscosity obtained ([η] 0.70 dl/g) was slightly less than that obtained previously ([η] 0.77 dl/g).

When the same procedures were followed but the final recrystallization from ethanol and resolution and recovery from methylene chloride were omitted (Table I, GL-6, -7), conversion was extremely low even after long polymerization times. It is, therefore, clear that the main reason for the relatively large amounts of catalyst previously required is the presence of ethanol in the monomer crystals which is not removed even after drying *in vacuo* ($10^{-6}$ mm) for 2 days.

Since the preceding experiments demonstrated no advantage for the use of acetyl fluoride, we reverted to our usual practice of using $PF_5$ alone. Polymerizations were run on monomer which had been carefully recrystallized at the bench from petroleum ether, and these were compared with like runs in which the monomer was dissolved and recovered from methylene chloride in the polymerization vessel. The results of the two series were indistinguishable (*cf.* Table II, GL15, 16, 17, 18) and both were substantially superior to any previous polymerizations in a number of ways.

It was found that the reaction could be speeded by running polymerizations at −55 to −60° instead of −70° (*cf.* GL8, 9, 10, 26, 27, 28, 30) with no loss in stereoregularity. (Products obtained from $PF_5$-catalyzed reactions at 0° are not stereospecific.)[3] The quantity of $PF_5$ could also be substantially reduced with completely reproducible results. Yields of 97% were obtained in 3 hr with 0.52 mol % catalyst (GL-17) and 92% in 4 hr with 0.26 mol % catalyst (GL-22). With smaller quantities of catalyst, reaction times were longer (GL23, 24, 25) and products were slightly lower in viscosity. However, conditions approaching our best consistently gave products of [η] 0.90–1.00 dl/g, values substantially higher than any obtained previously. These viscosities were still limited by chain transfer reactions because a two-stage polymerization in which a second batch of monomer was added to a polymerized sample resulted in additional polymerization without increase in molecular weight (GL-29). Furthermore, the molecular weight of products was independent of catalyst concentration in the range 0.3–1.3% while at lower con-

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TABLE I
POLYMERIZATIONS OF 1,6-ANHYDRO-2,3,4-TRI-*O*-BENZYL-β-D-GLUCOPYRANOSE[a]

| No. | Monomer, g | Catalyst,[a] mol % | Monomer to solvent ratio, g/100 ml | Temp, °C | Time, hr | Conversion, % | $[\alpha]^{25}D$,[a] deg | $[\eta]$[a] | $\bar{M}_n$ | $\overline{DP}_n$ |
|---|---|---|---|---|---|---|---|---|---|---|
| GL-1 | 0.89 | 2.8 | 39 | −78 | 100 | 91.7 | +113.2 | 0.28 | | |
| GL-2 | 0.89 | 2.0 | 36 | −78 | 97 | 93.5 | +113.5 | 0.39 | $8.82 \times 10^4$ | 219 |
| GL-3 | 2.79 | 0.99 | 48 | −78 | 24 | 37.3 | +113.2 | 0.67 | | |
| GL-4 | 4.70 | 0.44 | 57 | −78 | 101 | 59.8 | +113.5 | 0.70 | | |
| GL-5 | 4.80 | 0.40 | 57 | −60 | 48 | 95.6 | +113.7 | 0.69 | $1.65 \times 10^5$ | 381 |
| GL-6[b] | 5.0 | 0.40 | 45 | −60 | 168 | 24.3 | +113.3 | 0.60 | $1.15 \times 10^5$ | 265 |
| GL-7[b] | 5.0 | 0.30 | 43 | −60 | 168 | 2.5 | +113.2 | | | |

[a] Catalyst, $PF_5$–$CH_3COF$ (1:1); solvent for reaction, methylene chloride; solvent for $[\eta]$ determination, chloroform; solvent for $[\alpha]$ determination, chloroform (*c*, 1). [b] The monomer was neither recrystallized from ethyl alcohol under vacuum nor washed with methylene chloride. Monomer as used previously.

TABLE II
POLYMERIZATIONS OF 1,6-ANHYDRO-2,3,4-TRI-*O*-BENZYL-β-D-GLUCOPYRANOSE

| No. | $PF_5$, mol % | Monomer to solvent[a] ratio, g/100 ml | Time, hr | Conversion, % | $[\alpha]^{25}D$,[a] deg | $[\eta]$,[b] dl/g | $\bar{M}_n$ | $\overline{DP}_n$ |
|---|---|---|---|---|---|---|---|---|
| GL-8[c] | 1.3 | 50 | 0.3 | 38.4 | +113.2 | 1.00 | | |
| GL-9[e] | 1.3 | 50 | 0.7 | 83.4 | +113.4 | 0.99 | | |
| GL-10[c] | 1.3 | 50 | 3.5 | 99.0 | +114.0 | 0.93 | | |
| GL-11 | 1.2 | 50 | 0.8 | 81.4 | +113.7 | 1.02 | | |
| GL-12 | 0.99 | 50 | 0.8 | 77.5 | +113.3 | 1.09 | | |
| GL-13[i] | 0.81 | 50 | 1.2 | 95.2 | +113.4 | 1.00 | $3.52 \times 10^5$ | 813 |
| GL-14[i] | 0.64 | 50 | 0.8 | 90.5 | +113.3 | 0.98 | | |
| GL-15[i] | 0.52 | 100 | 0.3 | 41.4 | +113.7 | 1.04 (75%)<br>0.97 (25%) | $4.03 \times 10^5$ | 931 |
| GL-16 | 0.52 | 67 | 1.2 | 81.1 | +113.7 | 1.04 | $3.27 \times 10^5$ | 757 |
| GL-17[d] | 0.52 | 50 | 3.0 | 96.9 | +113.5 | 0.95 | $3.33 \times 10^5$ | 769 |
| GL-18[i] | 0.51 | 50 | 1.2 | 76.2 | +113.5 | 1.02 | | |
| GL-19[i] | 0.40 | 50 | 3.0 | 93.2 | +113.1 | 0.97 | $3.40 \times 10^5$ | 786 |
| GL-20[i] | 0.33 | 100 | 1.0 | 74.5 | +113.4 | 1.06 | $3.87 \times 10^5$ | 895 |
| GL-21[i] | 0.33 | 50 | 1.2 | 84.6 | +113.8 | 1.01 | $3.47 \times 10^5$ | 803 |
| GL-22[i] | 0.26 | 50 | 4.0 | 91.9 | +113.4 | 0.98 | | |
| GL-23[i] | 0.19 | 50 | 7.0 | 72.9 | +113.5 | 0.92 | $3.14 \times 10^5$ | 722 |
| GL-24[i] | 0.15 | 67 | 5.0 | 55.6 | +113.7 | 0.94 (90%)<br>0.89 (10%) | | |
| GL-25[e,i] | 0.10 | 50 | 40.0 | 44.5 | +113.5 | 0.86 | $2.94 \times 10^5$ | 680 |
| GL-24[f] | 1.3 | 50 | 0.3 | 6.8 | | | | |
| GL-27[f] | 1.3 | 50 | 0.7 | 18.4 | +112.4 | 1.02 | | |
| GL-28[f] | 1.3 | 50 | 3.5 | 70.0 | +113.8 | 0.84 | | |
| GL-29[g] | 0.65 | 50 | 3.0 | 75.8 | +113.9 | 0.74 | | |
| GL-30[h] | 0.82 | 50 | 3.3 | 93.5 | +113.4 | 0.80 | | |

[a] Reaction solvent, methylene chloride. Temperature, −60°. Monomer, 1-g scale. Solvent for $[\alpha]$, chloroform (*c* 1). [b] Determined in chloroform at 25°. [c] Monomer scale 0.5 g. [d] Monomer scale 5.0 g. [e] Monomer scale 1.9 g. [f] Polymerization temperature −70°. Monomer scale 0.5 g. [g] Monomer, 0.5 g, was polymerized with 1.3 mol % $PF_5$ for 40 min, and then an additional 0.5 g of monomer dissolved in 1.0 ml of $CH_2Cl_2$ was added to the polymerization solution. [h] Polymerization temperature −55°, monomer scale 3.0 g. [i] Monomer held in a polymerization ampoule was washed with $CH_2Cl_2$, recrystallized after removal of $CH_2Cl_2$, and dried under high vacuum.

centrations the molecular weight seemed to be less. This curious result may be due to traces of side reactions which occur during the longer polymerization times which are necessary to obtain high conversions. Polymers produced at −55° had slightly lower $\overline{DP}_n$ (GL-30).

Osmotic pressure measurements on unfractionated polymers gave molecular weights up to $3.87 \times 10^5$ ($\overline{DP}_n$ 895) and 75% of one preparation had a molecular weight $4.03 \times 10^5$ ($\overline{DP}_n$ 931). Unfractionated 2,3,4-tri-*O*-benzyl-[1→6]-α-glucopyranan prepared by this method and with $PF_5$–$CH_3COF$ complex catalyst followed the intrinsic viscosity–molecular weight relationship, $[\eta]_{CHCl_3} = 2.1 \times 10^{-4} \bar{M}_n^{0.66}$. It should be noted that this relationship need not hold for products with different molecular weight distributions, and indeed one of our products (GL-6) prepared from monomer which was not free from ethanol had a lower $\overline{DP}_n$ than that calculated from its intrinsic viscosity by this relationship.

In a previous publication,[5] we have reported that the polymerization of 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-galactopyranose is a much slower process than that of the glucose monomer and that the polymers are lower in molecular weight. By applying the refinements used above to the polymerization of the galactose derivative, the results reported in Table III were obtained. Again improvements were realized, but the general conclusions were confirmed. At all catalyst concentrations tried, conversion was still

TABLE III
POLYMERIZATIONS OF 1,6-ANHYDRO-2,3,4-TRI-*O*-BENZYL-β-D-GALACTOPYRANOSE[a]

| No. | $PF_5$, mol % | Monomer to solvent ratio, g/100 ml | Time, hr | Conversion, % | $[\alpha]^{25}D$, deg | $[\eta]$, dl/g | $\bar{M}_n$ | $\overline{DP}_n$ |
|---|---|---|---|---|---|---|---|---|
| GA-1[b] | 15.8 | 33 | 100 | 72.4 | +98.8 | 0.22 | $4.55 \times 10^4$ | 105 |
| GA-2[b] | 10.0 | 100 | 24 | 90.8 | +103.4 | 0.43 | $8.85 \times 10^4$ | 220 |
| GA-3[b] | 5.0 | 100 | 24 | 87.6 | +103.9 | 0.58 | $1.78 \times 10^5$ | 412 |
| GA-4[b] | 2.5 | 100 | 24 | 75.8 | +104.0 | 0.47 | $1.20 \times 10^5$ | 277 |
| GA-5[c] | 1.3 | 100 | 24 | 39.8 | +104.5 | 0.65 | $2.03 \times 10^5$ | 469 |
| GA-6[b] | 1.0 | 100 | 100 | 63.6 | +103.5 | 0.41 | $1.06 \times 10^5$ | 246 |
| GA-7[c] | 0.80 | 100 | 24 | 41.6 | +104.2 | 0.70 | $2.14 \times 10^5$ | 495 |
| GA-8[b] | 0.52 | 100 | 100 | 32.4 | +103.8 | 0.25 | $6.36 \times 10^4$ | 147 |
| GA-9[c] | 0.50 | 100 | 24 | 28.8 | +104.4 | 0.71 | $2.07 \times 10^5$ | 478 |
| GA-10[c] | 0.34 | 100 | 24 | 12.6 | +103.7 | 0.49 | $1.22 \times 10^5$ | 283 |

[a] Monomer recrystallized from petroleum ether. Temperature, −60°. Solvent, methylene chloride. [b] 1.0-g monomer scale. [c] 0.5-g monomer scale.

TABLE IV
DEBENZYLATIONS OF 2,3,4-TRI-*O*-BENZYL-[1→6]-α-D-GLUCOPYRANAN

| | Starting polymer | | | Reaction conditions | | Conversion, % | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| No. | Amt, g | $[\eta]$, dl/g | $(\overline{DP}_n)$ | Na, g | Time, hr | | $[\alpha]^{25}D$,[a] deg | $[\eta]$,[a] dl/g | $\bar{M}_n$[a] | $\overline{DP}_n$ |
| D-1[b] | 2.0 | 0.69 | (381) | 3.0 | 4.3 | 91.3 | +203.7 | 0.27 | $1.63 \times 10^4$ | 101 |
| D-2[b] | 2.5 | 0.95 | (769) | 3.7 | 4 | 84.6 | +204.3 | 0.29 | $2.42 \times 10^4$ | 149 |
| D-3 | 0.97 | 0.60 | (265) | 1.5 | 3 | 75.8 | +197.6 | 0.24 | $1.72 \times 10^4$ | 106 |
| D-4 | 0.87 | 0.98 | (776) | 1.5 | 4 | 96.0 | +200.7 | 0.38 | $2.31 \times 10^4$ | 143 |
| D-5 | 0.75 | 1.09 | (913) | 1.5 | 4 | 89.0 | +203.4 | 0.30 | $3.12 \times 10^4$ | 192 |
| D-6 | 0.87 | 0.49 | (273) | 1.5 | 3 | 93.9 | +201.2 | 0.42 | $2.66 \times 10^4$ | 164 |
| D-7 | 0.80 | 1.02 | (825) | 1.5 | 1 | 76.0 | +204.6 | 0.32 | | |
| | | | | | | | +178.0[c] | 0.21[c] | | |
| D-8 | 0.79 | 1.00 ~ 1.02 | | 0.6 | 2 | 88.8 | +206.0 | 0.41 | $2.69 \times 10^4$[d] | 166 |
| D-10[e] | 1.0 | 0.80 | (578) | 0.6 | 1.5 | 95.5 | +184.3[c] | 0.33[c] | | |
| D-11[e] | 1.0 | 0.80 | (578) | 0.4 | 1.5 | 97.3 | +187.2[c] | 0.37[c] | $4.28 \times 10^4$[d] | 264 |

[a] Determined in dimethyl sulfoxide (water content 0%), $[\alpha]/c$, 1 g/100 ml; $[\eta]$ at 25°; $\bar{M}_n$ (water content 0 ~ 0.2 vol %). [b] Liquid ammonia (200 ml) was used. [c] Determined in water. [d] Determined in 95 vol % dimethyl sulfoxide–5 vol % water mixture. [e] 1,2-Dimethoxyethane–toluene (1:1) mixture was employed for the solvent of the starting polymer.

incomplete and increasing even after 100 hr, in contrast to the case of glucose in which high conversions could be obtained in 1 hr or less. The highest molecular weight obtained was $2.14 \times 10^5$ ($\overline{DP}$ 495) for the polymer which was prepared with 0.8% catalyst over a period of 24 hr. In those polymerizations with long reaction times, the molecular weights of products were invariably lower than in similar runs made for a shorter period. It appears probable that the molecular weight loss is due to chain transfer processes. However, it is not clear whether chain scission of polymer occurs. An alternative explanation could be that as the monomer concentration and thus the rate of polymerization decrease, the probability of transfer of growing end to gegenion or other species increases. In any case, the choice of reaction time in this system involves a compromise between per cent conversion and $\overline{DP}$ of product.

The relationship between intrinsic viscosity and number-average molecular weight on these unfractionated samples of 2,3,4-tri-*O*-benzyl-[1→6]-α-D-galactopyranan is $[\eta]^{25}{}^{\circ}{}_{CHCl_3} = 5.2 \times 10^{-5}\bar{M}_n^{0.78}$. The same reservations must hold in the use of this relationship as in the use of that for the benzylated glucan.

Stereoregular linear [1→6]-α-D-gluco-, -manno-, and -galactopyranan have been prepared by debenzylating the corresponding benzyl ethers. Viscosities of the products indicated high molecular weights, but direct molecular weight measurements have not previously been made. A number of debenzylations of polymers of different molecular weights are reported in Table IV. Conversions of 76–97% were achieved. Specific rotations of 202° ± 4° were observed in dimethyl sulfoxide. The variability of these optical rotations (±2%) was greater than that of the benzylated polymers and probably reflects a somewhat variable water content, since we had difficulty in obtaining consistent carbon–hydrogen analyses. In any case, the values are in the range expected[15] for stereoregular polymer.

Molecular weights of the free polysaccharides, determined in dimethyl sulfoxide, ranged from $1.63 \times 10^4$ to $4.28 \times 10^4$ ($\overline{DP}$ 101–264). The benzyl ethers from which they were derived had $\overline{DP}$'s of 265–913. Apparently there are three or four chain scissions during the process of eliminating up to 2700 benzyl ether groups from the polysaccharide backbone. In general, shorter periods of time, smaller quantities of sodium, and perhaps the use of a mixture of 1,2-dimethoxyethane and toluene (1:1 v/v) resulted in somewhat higher molecular weight polysaccharides. Products obtained from reductions with lithium or potassium in liquid ammonia were poorer in quality.

Among these polysaccharides, there was no valid relationship relating intrinsic viscosity to number-average molecular weight. We assume that this indicates variations in molecular weight distributions in the products (*cf.* ref 16).

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## Experimental Section

**Synthesis of Monomers.** 1,6-Anhydro-2,3,4-tri-*O*-benzyl-β-D-gluco- and -galactopyranoses were synthesized as previously.[2,5,17] Final crystallizations of both monomers were preferably from petroleum ether (bp 30–60°). In the case of the glucose derivative, some samples were recrystallized last from ethanol, but then redissolved in the polymerization ampoule in methylene chloride, after which all the solvent was stripped off to remove adsorbed volatile impurities.

**Synthesis of Catalytic Complexes.** Complexes of $PF_5$ and acetyl fluoride (1:1 mole ratio) and of $SbF_5$ with benzoyl fluoride (1:1) were prepared entirely in a high-vacuum system by a modification of Olah's method.[14] Acetyl fluoride (Peninsular ChemResearch, Inc.), benzoyl fluoride (Aldrich Chemical Co.), and antimony pentafluoride (Ozark Mahoning Co.) were distilled a few times eliminating high and low cuts and finally transferred into calibrated microampoules with break-seals. Similar break-seals were prepared with *p*-chlorobenzenediazonium hexafluorophosphate (Ozark Mahoning Co.), and with Freon 12 to be used as solvent. Solvent, acyl halide, and Lewis acid break-seals were attached to a reaction vessel and their contents were transferred *in vacuo* into the reaction vessel in that order at liquid air temperature. (Lewis acids were both used in slight excess and phosphorus pentafluoride was generated by heating the diazonium salt.) After 30 min stirring at −60°, the Freon 12 was distilled off into the original ampoule, leaving behind a white $PF_5$–$CH_3COF$ complex or a slightly discolored $SbF_5$–$C_6H_5COF$ complex. Phosphorus pentafluoride complex could be conveniently prepared in $1 \times 10^{-4}$ mol quantities or greater and was subdivided by solution at room temperature in ~5 ml of $CH_2Cl_2$.

**Polymerization with $PF_5$–$CH_3COF$ (1:1) Complex Catalyst.** 1,6-Anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose (~5 g) was placed in one of two 100-ml flasks joined by a glass U tube with a sintered glass filter separating the two vessels. Pure ethanol (75 ml) was added, the solvent frozen, and the system evacuated. The monomer was dissolved with warming, filtered into second flask under vacuum, and allowed to crystallize. The mother liquor was transferred to the original flask for recovery of residue and the pure crystals were dried *in vacuo* for 2 days under high vacuum. From a stock solution (40 ml) of purified methylene chloride containing $5 \times 10^{-4}$ mol of $SbF_5$–$C_6H_5COF$ complex was distilled sufficient methylene chloride to dissolve the purified monomer. The monomer was recovered by evaporation of the methylene chloride, dried, and redissolved in enough methylene chloride for polymerization. This was transferred to a polymerization ampoule equipped with magnetic stirrer and catalyst ampoule. The reaction system was sealed off of the line, the entire system was immersed in a Dry Ice–isopropyl alcohol bath, and the catalyst break-seal was broken. The catalyst suspension was rapidly added to the monomer solution with stirring. All operations were carried out under glass *in vacuo*, until the polymerization was stopped with methanol. The usual washings, three precipitations in naphtha solvent, and freeze-drying from benzene gave products described in Table I.

**Polymerization with $PF_5$ Catalyst.** This method is described in detail elsewhere.[2,3] Only minor modifications obvious from the above text were used.

**Debenzylation of 2,3,4-Tri-*O*-benzyl-[1→6]-α-D-glucopyranan.** Our conventional technique using sodium and liquid ammonia was employed.[5,6] After 1~4.3 hr of reaction ammonium chloride was added until the blue color disappeared, preferably followed by addition of 30 ml of water. Elementary analysis showed that the polymers were ash free but had a variable $H_2O$ content.

**Molecular Weight Measurements.** A Hewlett-Packard Model 503 high-speed membrane osmometer was used for the measurements of number-average molecular weights. For the benzylated polymers, toluene was employed as solvent, while for polysaccharide pure dimethyl sulfoxide (water content 0–0.2 vol %) or 95 vol % dimethyl sulfoxide–5 vol % water mixture was used. The solvent mixture gave more consistent slopes to the $\pi/c$–$c$ plots than did DMSO alone. However, it appeared that the slope differences in fact produced little uncertainty in the molecular weight values. Since elementary analysis shows about 6% water content of the polysaccharide, the molecular weight corrected will be up to 6% less than the observed (Table IV), if it is corrected for water content.

Viscosities were determined at 25° by an Ubbelohde viscometer in chloroform for the benzylated polymers and in dimethyl sulfoxide (water content 0%) and/or in water for the polysaccharide.

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# Effect of Catalyst on the Stereoregularity of the Polymer Formed from Propene Sulfide

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ABSTRACT: Poly(propene-2-$d_1$ sulfide) has been prepared from propene-2-$d_1$ sulfide using eight catalysts including two which were partially stereoelective. The isotactic dyad contents were determined from the nmr spectra of the methylene protons and compared with those previously obtained using zinc and cadmium carbonates as catalysts. The isotactic dyad content ranged from nearly 100% for cadmium tartrate as catalyst to approximately 33% for triethyloxonium tetrafluoroborate as catalyst.

Previous work[2] has shown that the methylene protons in poly(propene-2-$d_1$ sulfide), made by polymerization of the cyclic sulfide, give rise to two overlapping AB quartets in the 100-MHz nmr spectrum. The two pairs of upfield B lines are coincident, but the two pairs of downfield A lines are resolved. There are thus two chemical shifts for the A protons, which have been assigned to isotactic dyads (downfield) and syndiotactic dyads (upfield). This assignment is supported by X-ray work[3] and by the spectra of the derived polysulfones.[4]

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