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 1×10^{-4} mol quantities or greater and was subdivided by solution at room temperature in $\sim$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 ($\sim$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 5×10^{-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 $1\sim4.3$ 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 π/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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TABLE I

PREPARATION[a] AND PROPERTIES OF POLY(PROPENE-2-d_1 SULFIDE)

Monomer, mmol	Catalyst and amount, mmol	Solvent, ml Toluene	Solvent, ml Heptane	Time, days	Yield, %	Isotactic, dyads, %	$[\eta]$,[i] ml g^{-1}	$10^{-5}M_n$[j]	Nature of polymer
8.8	0.19 cadmium *dl*-tartrate			17	100	>95	329	8.4	Hard
4.5	0.1 cadmium D-tartrate			3.5	39[d]	>95			Hard
10	0.9 $ZnEt_2$ + 0.9 H_2O	9	0.2	1	75	79	325	2.1	Hard
17.5	0.9 $ZnEt_2$ + 0.9 (−)DMBD[b]	18	0.2	2.7	30[e]	70	~430	5.4	Hard
4.5	0.1 zinc D-tartrate			15	44[f]	69			Hard
	Cadmium carbonate[c]					64			Hard
10	0.9 $ZnEt_2$ + 1.8 MeOH	9	0.2	6	80	55	246	2.0	Tacky elastomer
	Zinc carbonate[c]					55			Elastomer
19	1.12 $AlEt_3$ + 1.12 H_2O		2.3	6	70[g]	~50[h]			Tacky
10	0.5 Et_3OBF_4			1	100	~33			Soft tacky

[a] At room temperature. [b] *R*(−)-3,3-Dimethylbutane-1,2-diol. [c] References 2 and 4. [d] Only very slight optical activity in the polymer and residual monomer. [e] $[\alpha]^{25}D$ of polymer = 51.4° (in benzene); $[\alpha]^{25}D$ of residual monomer = −7.15° (neat). [f] $[\alpha]^{25}D$ of polymer = −5.8° (in benzene). [g] Including ~2% oligomer. [h] Amorphous component. [i] In benzene at 25°. [j] From osmotic measurements in toluene.

It was found[2b,4] that cadmium carbonate as catalyst gave a higher proportion of isotactic dyads (64%) than zinc carbonate (55%). This investigation has now been extended to other catalysts, in particular to cadmium tartrate, which, on the basis of both X-ray work[3] and the optical activity of polymer produced from optically active monomer,[5,6] was thought to give highly isotactic polymer.

Experimental Section

Monomer was prepared by the same method as before[2b] except that the conversion of propene oxide to propene sulfide was effected somewhat more efficiently by exchange with thiourea following the method of Bordwell and Andersen.[7]

Zinc diethyl (Orgmet Inc.) was supplied as a dilute solution in heptane. Aluminum triethyl (Schuchardt) was available in a metallic bottle and was distributed under vacuum into sealed tubes.

Catalysts were prepared from the metal alkyls by mixing appropriate amounts dissolved in heptane with 1 or 2 equiv of water, methanol, or *R*(−)-3,3-dimethylbutane-1,2-diol,[8] using a vacuum system, and stirring the mixture for 1–2 hr. The monomer was distilled in from an ampoule and the polymerization allowed to proceed at room temperature for 1 day or more.

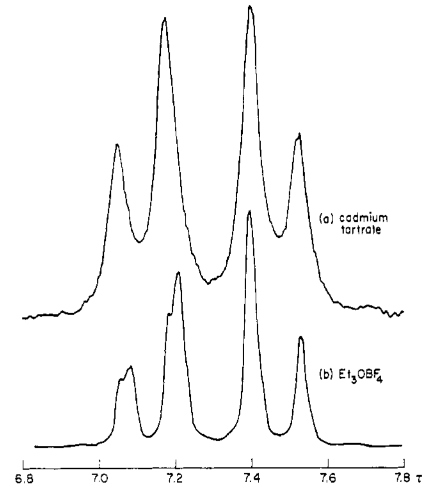

Figure 1. 100-MHz nmr spectra of poly(propene-2-d_1 sulfide) prepared using as initiator (a) cadmium tartrate and (b) triethyloxonium tetrafluoroborate. Solvent CCl_4, 25°.

Triethyloxonium tetrafluoroborate was freshly prepared from epichlorohydrin and boron trifluoride etherate; it was recrystallized from nitrobenzene under dry nitrogen before use.[9] Polymerizations were carried out in the absence of air; the catalyst was insoluble in the monomer.

Racemic and optically active tartrates were prepared by reaction between tartaric acid and the appropriate acetate in aqueous solution at 60°.[10]

Polymerizations were carried out in sealed tubes under vacuum, the catalyst being present as a finely divided solid. The products of each reaction were dissolved or diluted in benzene, precipitated by pouring into excess methanol, and dried in a vacuum desiccator.

Spectra were run on an HA-100 Varian spectrometer, in CCl_4 solution (6%) at 25° using TMS as internal reference (τ 10.00 ppm). The spectra were analyzed by means of a Du Pont 310 curve resolver.

Results and Discussion

The conditions of preparation and properties of the polymers are summarized in Table I. All polymers were prepared at room temperature and are listed in order of decreasing isotacticity.

Figure 1 shows the methylene spectra for the two extreme cases. The polymer made with cadmium tartrate as catalyst gave an almost perfectly symmetrical AB quartet, with lines in the positions previously assigned to the isotactic dyad;[2] this assignment is thereby confirmed since it is known that this polymer is isotactic.[3] This polymer was oxidized to the polysulfone and its spectrum, run in dimethyl-d_6-sulfoxide at 60°, was predominantly that of a single AB quartet, in the position expected.[4] It was estimated that the original polymer contained at least 95% isotactic dyads.

The polymer made with triethyloxonium tetrafluoroborate as catalyst contains more syndiotactic dyads than isotactic dyads. With this catalyst some head–head tail–tail structure might be expected on the basis of the evidence from optical rotation with other Friedel–Crafts catalysts.[5] The expanded spectrum did indeed show signs of small additional peaks compared with the other spectra. With the other catalysts it appears that the head–tail structure predominates.

The results in Table I show that the tacticity of the polymer depends on the nature of both the anion and the cation. Rather surprisingly, there is no significant degree of stereoelection with cadmium D-tartrate as catalyst even though the

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polymer produced is isotactic. Presumably with both cadmium D-tartrate and cadmium *dl*-tartrate there are two equally reactive types of site, one specific to the polymerization of the *R* monomer, the other to the polymerization of the *S* monomer. The polymer should therefore be racemic, *i.e.*, resolvable. With zinc D-tartrate, on the other hand, there is some degree of stereoelection, as also with ZnEt$_2$/(−)-DMBD. The isotactic dyad content of the polymers, however, is well below 100% and will be determined by a number of factors: (i) the number of types of catalyst site; (ii) the degree of stereoelection at each type of site; and (iii) the yield. More data are required before a correlation of optical activity and nmr data can be attempted. Knowing the specific rotation of the pure isomers (32.6°)[5,6] we may estimate that, in the experiment using ZnEt$_2$/(−)DMBD as catalyst, the average rate of polymerization of the *R* monomer is about three times that of the *S* monomer during the first 30% polymerization.

The polymer obtained using a mixture of aluminium triethyl and water as catalyst differed from the other polymers in that it contained a small amount of low molecular weight material which formed as small crystalline particles within the amorphous polymer. It was possible to separate these particles by hand with the aid of a needle. Molecular weight determinations indicated an approximately hexameric species,[11] giving sharp lines in the nmr spectrum. The spectrum of the main polymer showed slight contamination with this material but the isotactic dyad content could be seen to be approximately 50%.

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The Effect of Isomer Ratio on the Properties of Bis(4-aminocyclohexyl)methane Polyamides

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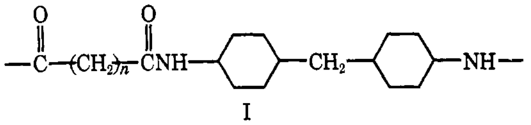
ABSTRACT: Differential thermal analysis data for bis(4-aminocyclohexyl)methane polyamides showed that glass transition temperatures and melting points increased with increasing trans,trans content of the diamine. These values all decreased with increasing chain length of the diacid used. There was also a polymerization rate dependence on the trans,trans content of the diamine. A conformational analysis based upon accessibility of the amino groups and relative stability of the various conformers was used to explain this rate phenomenon. X-Ray powder diagrams showed a change in interplanar spacings for the polyadipamides when the trans,trans diamine content reached 70%.

Bis(4-aminocyclohexyl)methane (PACM) can exist in three different geometric configurations, trans,trans (tt), cis,trans (ct), and cis,cis (cc). Each isomer would adopt a different configuration when incorporated in the backbone of a polyamide chain. This difference should be reflected in the polyamide properties, and the properties should vary with isomer content. There are several publications and patents on the polyamides of PACM,[1–10] but few discuss the effect of isomer ratio on polymer properties. In one paper it was shown that the softening temperatures of poly(PACM-adipamides) increased with increasing tt diamine content.[4] However, this was the only property discussed and none of the PACM samples contained more than 26 mol % of the tt diamine. The tt diamine has the highest degree of symmetry of the three isomers, and one would expect it to have the greatest effect upon the melting point, crystallinity, and glass transition temperature (T_c) of PACM-polyamides. It would be interesting to demonstrate this effect and also that of the chain length of the diacid on the properties of PACM-polyamides.

Discussion

We prepared three sets of polyamides from PACM samples of different isomer ratios and adipic, sebacic, and dodecanoic acids (Scheme I). The designations and isomer contents of the three PACM samples are as follows: PACM^1 51% tt, 40% ct, 9% cc, ±2%; PACM^2 70% tt, 25% ct, 5% cc, ±2%; PACM^3 98% tt, 2% ct, 0% cc, ±2%. PACM^1 is the normal hydrogenation product of 4,4′-diaminodiphenylmethane,[11] although other isomer mixtures could be obtained by changing the hydrogenation conditions.[12] PACM^2 was obtained by fractional crystallization of PACM^1 from *n*-

SCHEME I



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$^a n = 4, 8, 10.$

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