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Condensation Reactions

Synthesis of Polyterephthalates Derived from Dianhydrohexitols

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SUMMARY

By melting condensation of terephthalic acid dichloride and 1,4:3,6-dianhydrohexitols as well as selectively prepared lower oligomers thereof the formation of polyterephthalates is achieved. These polyesters are characterized by ^{1}H-NMR spectra vapour pressure osmometry (VPO), differential scanning calorimetry (DSC), viscosity measurements and combustion analyses. Their preparation and properties are discussed.

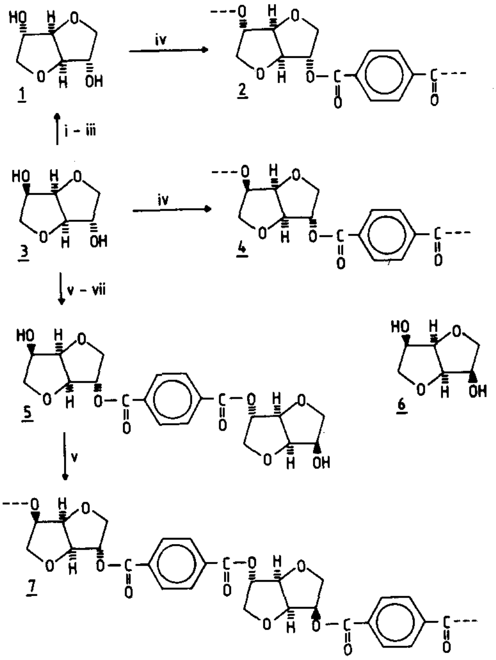
INTRODUCTION

Cost developments and accessibility of fossile raw materials as well as general long term arguments necessitate the exploition of available and hitherto unutilised regenerable carbon sources of the plant kingdom (1,2). Among others oligo- and polysaccharides like starch (3,4) and related carbohydrate derivatives represent an attractive basis for the generation of functionalised compounds which may be considered as starting materials or intermediates for various means and processes in chemical industries.

The polyol D-sorbitol obtained from starch by hydrolysis and subsequent hydrogenolysis is easily dehydrated to give (5,6) the crystalline, acid and thermostabile 1,4:3,6-dianhydro-D-sorbitol (DAS, 3). It is of interest to study the applications of this chiral, heterocyclic carbohydrate diol with (7R,8R)-cis-bicyclo[3.3.0]1,4-dioxaoctan framework for the synthesis of a new class of unbranched polyesters with a semi-natural/semi-synthetic structure.

RESULTS AND DISCUSSION

Melting condensation of DAS 3 with equimolar amounts of terephthalic acid dichloride (TADC) at 180°C led to a colourless amorphous material. This was dissolved in chloroform and dropwise added to methanol precipitating the partially crystalline polyester 4 (71% yield) and leaving the remaining lower oligomers and further contaminations in solution. The averarge number molecules weight of 3000 (vapour pressure osmometry) corresponds to a $\overline{DP} \approx 22$, and the chiral compounds showed an inherent viscosity $\eta_{inh} = 0.1213$ dl/g (at 40°C in m-Kresol). Its stereoirregularity could be assigned by n.m.r. signals of protons in the terephthalate moiety. All possible triads with a ratio of 3 : TADC = 2:1 or 1:2 were prepared and the chemical shifts and patterns of the aryl-protons assigned unequivocally (7). Thus in the ^{1}H-NMR spectrum of 4 both the symmetrical 2 → 2'-(δ 8.07 s, quasi A_4) and 5 → 5'-linkages (δ 8.17 s, quasi A_4) as well as the unsymmetrical 2 → 5'-linkage (δ 8.12 mc, AA'BB') of DAS residues via the terephthalate unit are documented by the appropriate signals (table 1). Using differential scanning calorimetry (DSC) 4 showed a T_g of 155°C and partial crystallinity with a T_{max} of 194°C. Material preheated above T_{max} and then quickly frozen to an amorphous polymer as expected showed a T_g on subsequent reheating. Then, after allowing the material to recrystallize a T_{max} could be observed again.



i) Ac_2O/Py (selective)
ii) $Ph_3P, EtO_2C-N=N-CO_2Et$, BzOH
iii) NaOMe/MeOH
iv) 1 equiv. $ClOC-C_6H_4-COCl$
v) oNBzCl/Py (selective)
vi) 0.5 equiv. $ClOC-C_6H_4-COCl$
vii) Zn/NH_4Cl; $THF-H_2O$

In contrast to DAS with its two different secondary hydroxy groups (*exo* at C-2 and *endo* at C-5) which consequently led to an irregular polyester the corresponding use of the symmetrical 1,4:3,6-dianhydro-D-mannitol (DAM, 6) (5) with both hydroxy group in *endo* position was of interest. However, 6 turned out to be too labile for a comparable melting condensation process at 180°C. Only 45% of polymer product obtained revealed a solubility in chloroform which points to the formation of crosslinked polymers. Obviously, under these conditions the anhydrorings in 6 may be partially ruptured which rules out its applications for the preparation of linear polyesters.

The third symmetrical dianhydrohexitol derivative is 1,4:3,6-dianhydro-L-iditol (DAI, 1) (5), which was favourably synthesized from DAS 3 by a three step procedure: 3 was selectively acetylated to give the 2-O-acetate (7,8), this inverted at C-5 to the 2-O-acetyl-5-O-benzoyl derivative of 1 (85%) following Mitsunobus method (9) and then deacylated to give 1. This educt under similar conditions gave the chiral polyterephthalate 2 (82%) with $\overline{M}_n \approx 3800$ ($\overline{DP} \approx 28$) and $\eta_{inh} = 0.1006$ dl/g and a stereoregular structure as evidenced by the aryl proton pattern (δ 8.07 s, A_4). Both the T_g as well as the T_{max} value of the partial crystalline polycondensate 2 correspond very much to those of the product 4.

Finally for comparison of chemical properties the availability of a stereoregular DAS polyterephthalate was of inter-

Table 1

Properties of Dianhydrohexitol Polyterephthalates

	2	4	7
yield (%)	82	71	80
T_{glas} (°C)	153	155	174
T_{max}(°C)	192	194	193
$[\alpha]_D^{20}$ ($CHCl_3$)	+182.3	- 65.5	- 73.3
$[\alpha]_D^{20}$(c 0.25 g/dl in m-Kresol, 40°C)	+241.6	-171.2	-193.2
η_{inh}(c 0.25 g/dl in m-Kresol, 40°C)	0.1006	0.1213	0.2688
$\overline{M}_n$	3800	3000	8000
^{1}H-NMR (270 MHz, $CDCl_3$) δ Aryl-H	8.07s	8.07s 8.12mc 8.17s	8.08s 8.17s
Anal. Calcd. for $(C_{14}H_{12}O_6)_x$(267.2) and $(C_{28}H_{24}O_{12})_x$(552.4)			
C, 60.87	Found: 60.11	60.08	60.06
H, 4.38	4.38	4.35	4.43

est. The synthesis of a starting diol from DAS 3 was achieved in three steps: first DAS was selectively esterified to give 1,4:3,6-dianhydro-5-O-o-nitrobenzoyl-D-sorbitol, then this in turn reacted with half a molar equivalent of TADC and finally the o-nitrobenzoate groups selectively cleaved by reduction under neutral conditions (10,11) to give the symmetrical triade 5 as a crystalline material. The subsequent polycondensation smoothly gave a polyester 7 (80%) with $\overline{M}_n \approx 8000$ ($\overline{DP} \approx 58$) and $\eta_{inh} = 0.2688$. As expected this chiral polymer showed the aryl proton pattern of symmetrical 2 → 2-(δ 8.08 s, A_4) and 5 → 5-linkages (δ 8.17 s, A_4) exclusively. With this compound 7 a quite increased $T_g = 174°C$ is observed whereas again the partial crystalline material showed a comparable $T_{max} = 193°C$.

Further studies on the technical applications of these and similar polycondensates and the influence of various chiral structural elements on the polymer properties are of interest.

EXPERIMENTAL

Di(1,4:3,6-dianhydro-D-sorbitol-2-yl)terephthalate (5):

Compound 3 (15.0 g, 0.1 mol) dissolved in abs pyridin (150 ml) is added dropwise under cooling (-10°C) to o-nitrobenzoylchloride (18.0 g, 0.1 mol) and stirred at room temperature for 2 d. The solvent is removed in vacuo and the residue purified by column chromatography (silica gel G 60, Merk, ethylacetate/n-hexane 3:1). The second fraction gives 9.7 g (66%) 1,4:3,6-dianhydro-5-O-o-nitrobenzoyl-D-sorbitol; m.p. 123°C, $[\alpha]_D^{20}$ +6.0 (c 0.81, ethyl acetate). Anal. calcd. for $C_{13}H_{13}NO_7$ (295.2): C, 52.89; H, 4.44; N, 4.74. Found: C, 52.91; H, 4.56; N, 4.51.

This material (5.4 g, 18 mmol) and terephthalic acid dichloride (1.8 g, 9 mmol) are quickly heated to 180°C under efficient stirring and exclusion of moisture. After hydrogen chloride evolution has ceased the mixture is stirred another 10 min, cooled and purified by column chromatography (ethyl acetate/n-hexan 3:1) to give 5.6 g (86%) di(1,4:3,6-dianhydro-5-O-ortho-nitrobenzoyl-D-sorbitol)terephthalate; m.p. 78°C, $[\alpha]_D^{20}$ -37.7 (c 0.45, dichloromethane). Anal. Calcd. for $C_{34}H_{28}N_2O_{16}$ (720.6): C, 56.67; H, 3.92; N, 3.89. Found: C, 56.42; H, 4.09; N, 3.89.

The latter compound (5.0 g, 6.9 mmol) together with ammonium chloride (5.35 g, 100 mmol) is dissolved in tetrahydrofuran/water (2:1 v/v) and efficiently stirred with zink dust (2.0 g, 30 mmol) for 24 h. The solvents are evaporated. the residue taken up in dichloromethane, concentrated and purified by column chromatography (ethyl acetate) to give

1.52 g (52%) of 5; m.p. 161.0°C, $[\alpha]_D^{20}$ +77.9 (c 0.7, chloroform). Anal. calcd. for $C_{20}H_{22}O_{10}$ (422.4): C, 56.87; H, 5.25. Found: C, 56.83; H, 5.46.

Polycondensation procedure:

Equimolar amounts of the diol component and TADC are rapidly heated to 180°C under efficient stirring and rigorous exclusion of moisture. After 5 min at normal pressure the melt is treated another 5 min at reduced pressure (20 mm Hg). The cooled material is obtained as a colourless, glas-like, brittle polyester in quantitative yields. Purification of the polymer is performed by adding dropwise the chloroform solution of this raw material to methanol. By-products and oligomers remain dissolved whereas the pure polyester precipitates and is dried and further characterized successively.

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