polymer report

Synthesis and properties of polyesters based on 2,5-furandicarboxylic acid and 1,4:3,6-dianhydrohexitols

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Polyesters derived from 2,5-furandicarboxylic acid and 1,4:3,6-dianhydrohexitols have been prepared. These polyesters are made solely from monomers derived from renewable resources such as starch and fructose. As shown by thermogravimetric analysis, all materials have excellent stability against thermal decomposition. For sufficient degrees of polymerization, the glass transition of these polyesters, as determined by differential scanning calorimetry, is about 185°C. The degree of crystallinity, as studied by wide-angle X-ray scattering, is low for all materials investigated.

(Keywords: synthesis; properties; polyesters)

INTRODUCTION

The overwhelming majority of polymers used for technical purposes are made from oil-based monomers. Polymers derived from starch or related carbohydrates would be a very interesting goal since these materials can be made from entirely renewable resources[1–3]. The direct use of monomeric carbohydrate derivatives is extremely difficult, however, as the large number of hydroxy functionalities in these compounds renders the synthesis of well-defined products a very difficult task. This problem can be circumvented using 1,4:3,6-dianhydrohexitols for the synthesis of polyesters[4–6], because these compounds bear only two hydroxy groups and exhibit sufficient thermal stability[7]. Polycondensation of these diols with terephthaloyl dichloride under mild reaction conditions leads to well-defined, high-molecular-weight and thermally stable polymers[8].

We present here a systematic study of polyesters **2**, **3**, and **4**, which are derived entirely from renewable resources. They are made from 2,5-furandicarbonyl dichloride, **1**, and three different dianhydrohexitols, namely 1,4:3,6-dianhydro-D-sorbitol (DAS), 1,4:3,6-dianhydro-D-mannitol (DAM) and 1,4:3,6-dianhydro-L-iditol (DAI) (*Scheme 1*). The furan derivative is available from D-fructose in technical quantities through a two-step procedure[9,10]. The latter monomer has previously been used for the synthesis of polyamides and polyesters[11–23].

All polycondensations were carried out in solution. The thermal behaviour of the obtained polyesters **2**, **3** and **4** was investigated by thermogravimetric analysis (t.g.a.) and by differential scanning calorimetry (d.s.c.). The structures in the solid state were surveyed qualitatively by wide-angle X-ray scattering (WAXS).

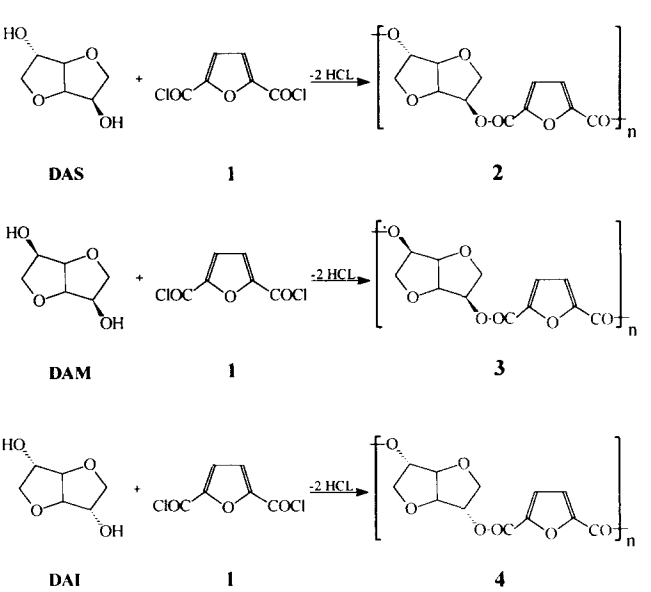
EXPERIMENTAL

Materials

All chemicals and solvents were purchased from Fluka or Aldrich. Pyridine was dried by refluxing over metallic sodium/benzophenone followed by distillation under an atmosphere of nitrogen. 1,1,2,2-Tetrachloroethane was refluxed with calcium chloride and fractionally distilled. 2,5-Furandicarboxylic acid was a gift from Südzucker. The acid dichloride was prepared with thionyl chloride, as described in the literature[24]. It was purified carefully by repeated sublimation. DAS was a gift from Cerestar, DAM was purchased from Aldrich, and DAI was synthesized according to the method of Thiem and Bachmann[25]. All diols were purified by repeated recrystallization from ethyl acetate and subsequently dried in the molten state *in vacuo* (0.01 mbar). All reactions were carried out under an atmosphere of nitrogen.

Methods

^{1}H n.m.r. spectra were recorded at 400 MHz and ^{13}C n.m.r. spectra at 100 MHz, using a Bruker AM 400 *FT* n.m.r. spectrometer. Tetramethylsilane served as an internal standard. Membrane osmometry measurements were carried out using a Knauer membrane osmometer 01.00. WAXS was monitored using Ni-filtered CuKα



Scheme 1

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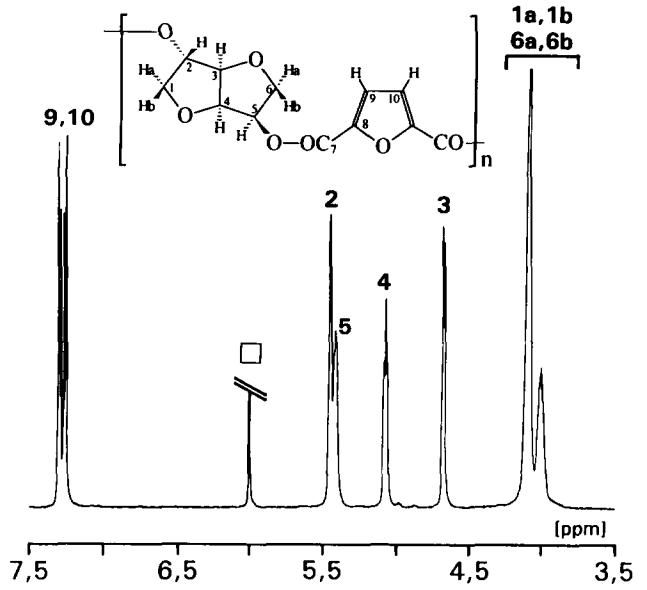

Figure 1 ^{1}H n.m.r. spectrum of polyester **2c** recorded in $C_2D_2Cl_4$ (□) at 400 MHz

radiation in reflection mode (Siemens D-5000). The intrinsic viscosities of the polyesters were determined using Ubbelohde capillary viscosimeters. For gel permeation chromatography (g.p.c.), 5 μm Styragel columns (10^5 and 10^3 Å, Polymer Standard Service, Mainz, Germany) were used with chloroform (1 ml min^{-1}) as the mobile phase (u.v. detection at $\lambda = 254$ nm). D.s.c. was done with a Mettler DSC-30 calibrated with indium and tin. T.g.a. data were obtained by means of a Netzsch STA 409 under an atmosphere of oxygen or nitrogen employing a heating rate of 10 K min^{-1}.

Synthesis of the polyesters

General procedure. Dianhydrohexitol (5.0 g, 34.21 mmol) and 2,5-furandicarbonyl dichloride (6.6 g, 34.21 mmol) were dissolved in 1,1,2,2-tetrachloroethane (17 ml). Both compounds were dissolved by vigorous stirring and slight warming. After complete dissolution, the solution was cooled to 0°C. Pyridine (22 ml) was added dropwise with vigorous stirring, and 10 min later a further portion of 1,1,2,2-tetrachloroethane (5–10 ml) was added. The temperature was then raised to 25°C and stirring was continued for 24 h. An additional portion of 2,5-furandicarbonyl dichloride (0.033 g, 0.17 mmol) was added after this time, and a second portion after 48 h. After 4 days of stirring the mixture was poured into an excess of methanol (2 l). The precipitated polymer was filtered off and washed carefully with methanol. The raw product was purified by redissolving in 1,1,2,2-tetrachloroethane and subsequent precipitation into methanol. The fibrous polyester was dried *in vacuo* (60°C, 0.01 mbar). Yield: 6.83–7.74 g (75–85%).

Polyester 2. ^{1}H n.m.r. ($C_2D_2Cl_4$). δ (ppm): 3.99–4.09 (m; 4H, H^{1a}, H^{1b}, H^{6a}, H^{6b}), 4.67 (m; 1H, H^3), 5.07 (m; 1H, H^4), 5.41 (m; 1H, H^5), 5.45 (m; 1H, H^2), 7.25–7.30 (m; 2H, H^9, H^{10}).

^{13}C n.m.r. ($C_2D_2Cl_4$). δ (ppm): 71.14 (t; C^6), 73.45 (t; C^1), 75.35 (d; C^4), 79.26 (d; C^3), 81.34 (d; C^5), 86.16 (d; C^2), 119.66 (d; C^9, C^{10}), 146.40, 146.54, 146.68 (3s; C^8), 157.20, 157.43 (2s; C^7).

$(C_{12}H_{10}O_7)_n$ $(266.2)_n$. Calculated: C 54.14, H 3.79; found: C 53.21, H 3.81.

Polyester 3. ^{1}H n.m.r. ($C_2D_2Cl_4$). δ (ppm): 4.07 (m; 4H, H^{1a}, H^{1b}, H^{6a}, H^{6b}), 4.88 (d; 2H, H^3, H^4), 5.30 (m; 2H, H^2, H^5), 7.35 (s; 2H, H^9, H^{10}).

^{13}C n.m.r. ($C_2D_2Cl_4$). δ (ppm): 70.81 (t; C^1, C^6), 74.95 (d; C^3, C^4), 80.69 (d; C^2, C^5), 119.82 (d; C^9, C^{10}), 146.50 (s; C^8), 157.55 (s; C^7).

$(C_{12}H_{10}O_7)_n$ $(266.2)_n$. Calculated: C 54.14, H 3.79; found: C 53.11, H 3.72.

Polyester 4. ^{1}H n.m.r. ($C_2D_2Cl_4$). δ (ppm): 4.08 (m; 4H, H^{1a}, H^{1b}, H^{6a}, H^{6b}), 4.87 (s; 2H, H^3, H^4), 5.44 (m; 2H, H^2, H^5), 7.27 (s; 2H, H^9, H^{10}).

^{13}C n.m.r. ($C_2D_2Cl_4$). δ (ppm): 72.73 (t; C^1, C^6), 79.02 (d; C^3, C^4), 85.64 (d; C^2, C^5), 119.89 (d; C^9, C^{10}), 146.61 (s; C^8), 157.17 (s; C^7).

$(C_{12}H_{10}O_7)_n$ $(266.2)_n$. Calculated: C 54.14, H 3.79; found: C 53.08, H 3.80.

RESULTS AND DISCUSSION

Polymer synthesis

Solution polycondensation of 2,5-furandicarboxyl dichloride and the respective 1,4:3,6-dianhydrohexitol in 1,1,2,2-tetrachloroethane in the presence of pyridine led to colourless, fibrous polyesters. The method of polycondensation chosen yields products with high degrees of polymerization. It should be noted that the 2,5-furandicarbonyl dichloride is extremely sensitive towards side reactions, in particular hydrolysis. To achieve an optimum degree of polymerization, 2,5-furandicarbonyl dichloride was used in a small excess and therefore further small amounts of this compound were added twice during the reaction. Another problem is the strong tendency for side reactions when the reaction is run at higher temperatures. Here, only strongly discoloured products with low molecular weights were obtained. Side reactions were also observed when a stronger base, such as triethylamine, was used instead of pyridine. If the conditions for polycondensation are chosen properly, however, degrees of polymerization of the order of 80–90 were reached without difficulty (see below).

Characterization in solution

All polyesters described herein exhibit a good solubility in 1,1,2,2-tetrachloroethane or dimethyl sulfoxide. Solutions in *N,N*-dimethylformamide or chloroform tend to form gels, particularly at higher concentrations. The sufficient solubility of the polyesters in common solvents allows comprehensive analysis by n.m.r. methods. *Figure 1* displays the ^{1}H n.m.r. spectrum of polyester **2c** and *Figure 2* the respective ^{13}C n.m.r.

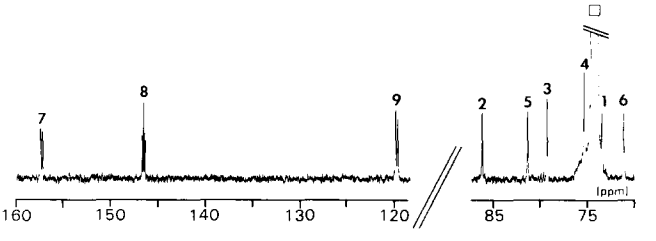

Figure 2 ^{13}C n.m.r. spectrum of polyester **2c** recorded in $C_2D_2Cl_4$ (□) at 100 MHz

Table 1 Characterization of polyesters **2–4**

Polyester	M_n[a] (g mol^{-1})	DP	$[\eta]$ (dl g^{-1})	T_g (°C)	T.g.a. (°C) (air/N_2)
2a	9000	34	0.11[b]	173	–
2b	22500	85	0.35[b]	190	–
2c	25000	94	0.38[b]	194	320/340
3a	14900	56	0.16[c]	187	–
3b	20400	77	0.22[c]	191	340/350
4	21500	81	0.22[c]	196	300/320

[a] Determined by membrane osmometry in 1,1,2,2-tetrachloroethane, 30°C
[b] Determined in *N*,*N*-dimethylformamide, 30°C
[c] Determined in 1,1,2,2-tetrachloroethane, 30°C

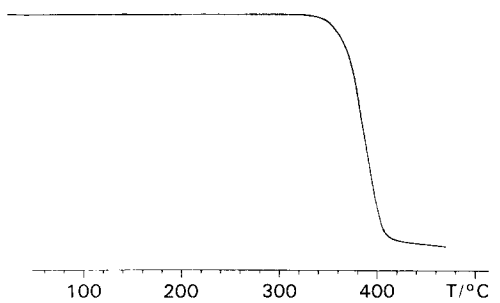

Figure 3 Thermogravimetric analysis of polyester **2c** conducted under an atmosphere of oxygen with a heating rate of 10 K min^{-1}

spectrum. The signals were assigned using the spectra of the respective monomers and by selective decoupling experiments. All observed signals occurring in these spectra can be related unambiguously to the corresponding repeating units.

In the ^{13}C n.m.r. spectrum, all absorptions of the furanic units are split, pointing to a slightly different chemical environment. This is caused by the chiral DAS bearing two different secondary hydroxy groups. Depending on the type of connection with the two adjacent hexitol moieties (endo→endo, exo→exo, endo→exo), absorptions at slightly different δ-values were found, in agreement with earlier observations[4,8]. This observation confirms the formation of a stereo-irregular polyester, despite the fact that the reactivity of the two hydroxy groups of DAS is different[26,27]. As expected, the absorptions of polyesters **3** and **4** made from hexitols with two identical hydroxy groups (DAM: endo at C^2 and C^5; DAI: exo at C^2 and C^5) do not show any splitting (see Experimental section). Except for the low-molecular-weight polyester **2a** there are no additional absorptions that point towards endgroups or structural irregularities.

The satisfactory solubility of the polymers in common organic solvents allowed the molecular weights to be determined by membrane osmometry in 1,1,2,2-tetrachloroethane at 30°C. *Table 1* summarizes the results together with the respective intrinsic viscosities. Analysis by g.p.c. furthermore showed the molecular weight distribution to be unimodal.

In conclusion, neither the ^1H nor the ^{13}C n.m.r. spectra show any evidence for structural defects in the polyesters presented here. It is therefore evident that the method of polycondensation employed herein proceeds practically without side reactions. This conclusion is corroborated by the satisfactory molecular weights (see *Table 1*).

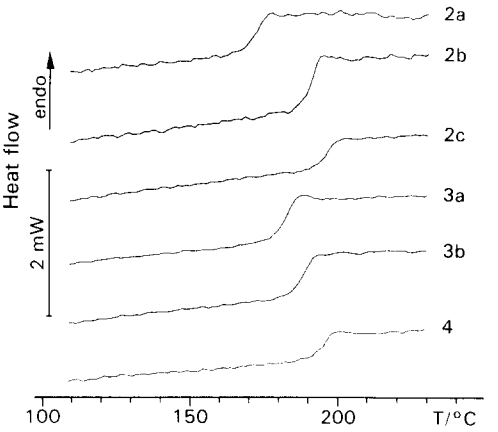

Figure 4 Thermal analyses of the annealed polyesters **2–4** conducted with a heating rate of 10 K min^{-1}

Thermal behaviour and structure

A primary concern in the study of thermal behaviour and possible technical applications of polyesters **2–4** is their stability at elevated temperatures. T.g.a. under nitrogen, as well as under air, proves these materials to be stable up to temperatures above 300°C; the data are given in *Table 1*. *Figure 3* shows an example of the t.g.a. of polyester **2c**.

All polyesters exhibit a rather high glass transition temperature, T_g, as shown in *Figure 4* (see also *Table 1*). A similar range of T_g values has been found in the case of polyesters made from DAS and terephthalic acid[8], and can be traced back to the intrinsic stiffness of the polymer chain. A first survey of the structures in the solid state by WAXS demonstrates that all materials exhibit a very low degree of crystallinity.

CONCLUSION

This investigation has shown that polyesters with good thermal stability, as well as high glass transition temperatures, can be made solely from monomers based on renewable resources. Since 2,5-furandicarboxylic acid and 1,4:3,6-dianhydro-D-sorbitol are available in industrial bulk quantities, these polyesters represent a step towards technical polymers derived entirely from such ubiquitous resources as starch or fructose.

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