

# Synthesis and Thermal Analysis of Copolyesters Deriving from 1,4:3,6-Dianhydrosorbitol, Ethylene Glycol, and Terephthalic Acid

The synthesis and analysis of copolyesters based on 1,4:3,6-dianhydrosorbitol (DAS), ethylene glycol, and terephthalic acid is described. It is shown that these copolyesters present materials stable up to elevated temperatures. The glass transition temperature,  $T_g$ , is shown to rise linearly with increasing content of DAS to reach values well above 100°C. Thus, DAS derived from renewable resources is a highly interesting diol component for making technical polyesters.

## INTRODUCTION

The synthesis of polymers from raw materials based on renewable resources, such as starch or cellulose, presents an important challenge because these two polysaccharides are available in nearly limitless quantities.<sup>1-3</sup> Very often research<sup>4</sup> in this regard is directed toward biodegradable polymeric materials that may be used for food packaging. In recent years it has been demonstrated, however, that starch may be converted to yield monomers that may be used for the synthesis of well-defined polyesters,<sup>5-8</sup> polyamides,<sup>9</sup> and polyurethanes.<sup>10</sup> In particular, polyesters containing 1,4:3,6-dianhydrosorbitol (DAS) could be shown<sup>7,8</sup> to be thermally stable up to high temperatures. The high glass transition temperature,  $T_g$ , of polyesters derived from DAS and terephthalic acid is around 200°C if molecular weights are high enough.<sup>7</sup> The main reason for this finding is the stiff bicyclic structure of DAS that does not allow for internal rotatory degrees of freedom. Because DAS is available in industrial quantities,<sup>11,12</sup> it presents an interesting diol component for the synthesis of polyesters.

Thus, in extension of earlier work<sup>7,8</sup> we present here a study of copolyesters derived from ethylene glycol, DAS, and terephthalic acid. These materials were prepared by polycondensation of the diols and terephthalic acid dichloride (TDC) in solution. This method of synthesis has been shown recently<sup>7,8</sup> to yield the highest molecular weights (Scheme 1). The main goal is the modification of poly(ethylene terephthalate) (PET) by incorporation of DAS moieties in order to obtain materials with elevated glass temperatures.

## EXPERIMENTAL

### Materials

All chemicals were purchased from Merck or Fluka. All solvents used were of analytical quality unless otherwise

stated. Toluene, ethylene glycol, and pyridine (Fluka) were dried by refluxing over metallic sodium/benzophenone under an atmosphere of nitrogen. TDC was sublimated prior to use. 1,4:3,6-Dianhydro-D-sorbitol was a gift from Cerestar. It was purified carefully by repeated recrystallization from ethyl acetate and subsequent drying in the molten state in vacuo (0.1 mbar). All reactions were carried out under an atmosphere of nitrogen.

### Measurements

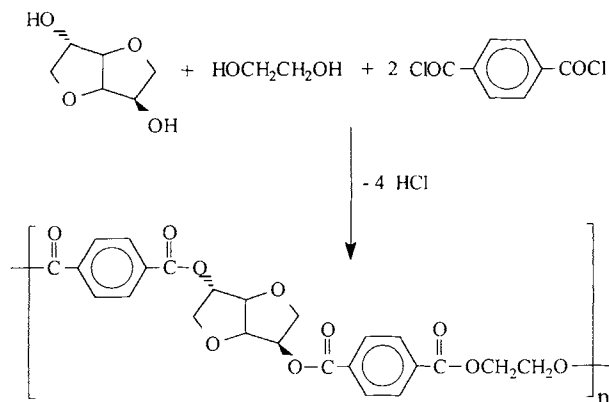
<sup>1</sup>H-NMR spectra were recorded at 400 MHz and <sup>13</sup>C-NMR spectra at 100 MHz, using a Bruker AM 400 FT NMR spectrometer. Tetramethyl silane was used as internal standard. Differential scanning calorimetry (DSC) was done with a Mettler DSC-30 calibrated with indium and tin. Thermogravimetric data were obtained by means of a Netzsch STA 409 under an atmosphere of nitrogen employing a heating rate of 10 K min<sup>-1</sup>. The intrinsic viscosities of the polyesters were determined using an Ubbelohde capillary viscosimeter. Wide-angle X-ray analysis (WAXS) was performed using Ni-filtered Cu-K $\alpha$  radiation in reflection mode using a Siemens D-5000 diffractometer.

### Preparation of Copolyesters 1-5

Respective amounts of DAS, ethylene glycol, and terephthaloyl dichloride (cf. Table I) were dissolved in toluene at 90°C to obtain a 40% solution. A fourfold excess of pyridine was added dropwise within a 20 min period of time. After heating and stirring for 2 days at 90–100°C, the reaction mixture was poured into methanol. The precipitate was collected by filtration and dried in vacuo (0.1 mbar). Yield: Almost quantitative.

PET <sup>1</sup>H-NMR (C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>):  $\delta$  = 4.67 (s; 4H, —(CH<sub>2</sub>)<sub>2</sub>—), 8.09 (s; 4H, Aryl-H). <sup>13</sup>C-NMR (C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>):  $\delta$  = 63.37 (t; (CH<sub>2</sub>)<sub>2</sub>), 130.05 (d; Aryl), 133.89 (s; CO-Aryl), 165.78 (s; C=O).

Copolyester DAS/Ethylene Glycol/TDC (Scheme 2) <sup>1</sup>H-NMR (C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>):  $\delta$  = 4.09–4.13 (m; 4H, H<sup>a</sup>, H<sup>b</sup>, H<sup>6a</sup>, H<sup>6b</sup>), 4.685 (s; 4H, H<sup>11</sup>), 4.689 (m; 1H, H<sup>3</sup>), 5.09 (m; 1H, H<sup>4</sup>), 5.43 (m; 1H, H<sup>5</sup>), 5.48 (m; 1H, H<sup>2</sup>), 8.08–8.16 (m; 4H, H<sup>9</sup>, H<sup>10</sup>). <sup>13</sup>C-NMR (C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>):  $\delta$  = 63.39 (t; C<sup>11</sup>), 71.27 (t; C<sup>6</sup>), 73.44 (t; C<sup>1</sup>), 75.26 (d; C<sup>4</sup>), 79.03 (d; C<sup>3</sup>), 81.39 (d; C<sup>5</sup>), 86.28 (d; C<sup>2</sup>),



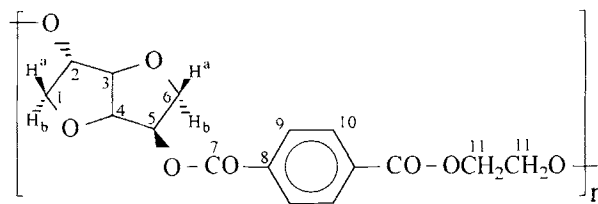
Scheme 1

130.11 (d; C<sup>9</sup>, C<sup>10</sup>), 133.53–134.13 (m; C<sup>8</sup>), 165.03, 165.33, 165.79 (3d; C<sup>7</sup>).

## RESULTS AND DISCUSSION

All copolyesters can be dissolved easily in a mixture of trifluoroacetic acid and methylene chloride (1 : 4), in *m*-cresol, or in 1,1,2,2-tetrachloroethane. Materials with a higher content of DAS (>20%) are soluble as well in *N*-methyl pyrrolidone and *N,N*-dimethylformamide; they cannot be dissolved in chloroform or *o*-dichlorobenzene, however.

The good solubility allows the full characterization of the copolyesters by <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectroscopy. The correct structure of the copolyester chain is proven directly by these measurements. Also, the integration of the signals pertaining to the respective components corresponds to the stoichiometric amounts.



Scheme 2

To check the thermal stability, samples of copolyesters were heated to 280°C for 15 min, cooled down to room temperature again, and analyzed by <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectroscopy. There was no indication for degradation within given limits of error.

Because the copolyesters under consideration here do not dissolve in solvents suitable for osmometric measurements, no absolute figures with regard to molecular weight can be given. Therefore Table I gathers only the intrinsic viscosities determined in suitable solvents.

As is obvious from these data, there is a slight increase of the intrinsic viscosities with increasing content of DAS, which might point to higher molecular weights. Because the polycondensation was conducted under the same conditions for all compositions, a more feasible explanation may be sought in the spatial extension of the chains by the incorporation of more and more DAS moieties, for example, with an increase of the Kuhn length due to the presence of more and more extended rigid units.

From a comparison of the magnitude of the intrinsic viscosities of the copolyesters with the respective data of the homopolyesters studied by Storbeck et al.,<sup>7</sup> all materials can be at least estimated to have degrees of polymerization of the order of 50. As has been shown for the homopolyesters,<sup>7,8</sup> such degrees of polymerization are high enough to ensure minimization of the influence of end groups, in particular when discussing *T<sub>g</sub>*.

**Table I** Characterization of Copolyesters Consisting of DAS, Ethylene Glycol, and Terephthalic Acid

| Polyester            | Content DAS (%) | $[\eta]^a$ (cm <sup>3</sup> g <sup>-1</sup> ) | $[\eta]^b$ (cm <sup>3</sup> g <sup>-1</sup> ) | $[\eta]^c$ (cm <sup>3</sup> g <sup>-1</sup> ) | <i>T<sub>m</sub></i> <sup>d</sup> (°C) | <i>T<sub>g</sub></i> <sup>d</sup> (°C) |
|----------------------|-----------------|---|---|---|--|--|
| PET <sup>e</sup>     | 0               | —   | 22.6  | 24.4  | 261                                    | 85                                     |
| <b>1</b>             | 10.3            | —   | 27.9  | 29.4  | 231                                    | 90                                     |
| <b>2</b>             | 20.0            | 27.1  | 32.9  | —   | 221                                    | 103                                    |
| <b>3</b>             | 34.3            | 32.2  | —   | —   | —                                      | 115                                    |
| <b>4</b>             | 50.6            | 46.4  | —   | —   | —                                      | 140                                    |
| <b>5</b>             | 81.1            | 42.2  | —   | —   | —                                      | 178                                    |
| DAS/TDC <sup>f</sup> | 100             | 41.4  | —   | —   | —                                      | 197                                    |

<sup>a</sup> Measured in *N*-methylpyrrolidone at 30°C.

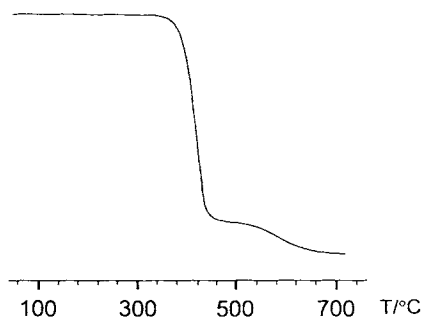
<sup>b</sup> Measured in *m*-cresol at 30°C.

<sup>c</sup> Measured in CF<sub>3</sub>COOH/CH<sub>2</sub>Cl<sub>2</sub> (1 : 4) at 30°C.

<sup>d</sup> Determined by DSC at a heating rate of 10 K min<sup>-1</sup> under an atmosphere of nitrogen.

<sup>e</sup> Poly(ethylene terephthalate).

<sup>f</sup> Polyester from DAS and terephthalic acid, data taken from Storbeck et al.<sup>7</sup> The intrinsic viscosity of this sample corresponds to a molecular weight of 14,200 g/mol, i.e., a degree of polymerization of 51.



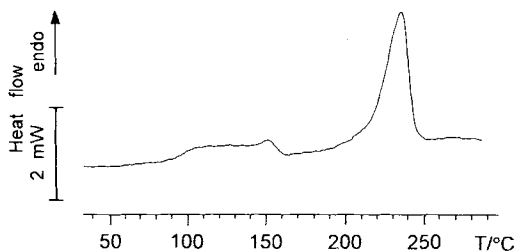
**Figure 1** Thermogravimetric analysis of copolyester 4 (cf. Table I) under an atmosphere of nitrogen and a heating rate of  $1 \text{ K min}^{-1}$ .

An important prerequisite for technical use of such materials is a sufficient thermal stability at elevated temperatures. Figure 1 shows the thermogravimetric analysis of copolyester 4 (cf. Table I) conducted at  $10 \text{ K min}^{-1}$  under an atmosphere of nitrogen.

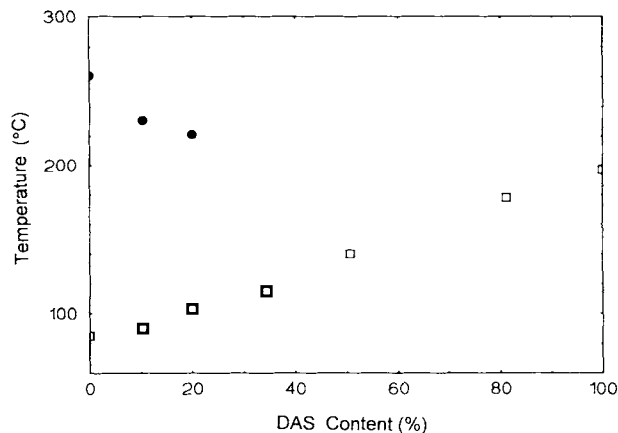
Under these conditions the materials are stable up to ca.  $300^\circ\text{C}$ . A similar finding was reported<sup>7,8</sup> previously for other polyesters containing DAS. The good stability, even at high temperature, therefore allows the study of these materials by thermal analysis (DSC). All DSC runs were conducted at a  $10 \text{ K min}^{-1}$ ; a typical run is displayed in Figure 2 showing a melting endotherm and a glass transition.

The respective glass transition temperatures as well as the melting points of the materials are shown in Figure 3. Up to a DAS content of 20%, the copolyesters are semicrystalline. If more and more DAS units are built in the chain the crystallization is suppressed. This is evident from the respective DSC traces showing only a glass transition, and can be directly corroborated by the WAXS analysis that confirms the amorphous structure of these materials. The asymmetric DAS units obviously have a strong tendency to suppress crystallization. This is in agreement with the previous analysis<sup>7</sup> of homopolyesters composed of DAS and terephthalic acid. Here also it could be shown by DSC and WAXS that these materials are amorphous and will not crystallize from the melt.

The marked lowering of the melting transition even at small DAS content points in the same direction. It fur-



**Figure 2** DSC run of copolyester 1 conducted under an atmosphere of nitrogen at a heating rate of  $10 \text{ K min}^{-1}$ .



**Figure 3** (●) Melting temperatures and (□) glass transition temperatures of the copolyesters as function of molar content of DAS. All data were determined by DSC runs (cf. Fig. 3) at a heating rate of  $10 \text{ K min}^{-1}$ .

thermore suggests that there is no extensive formation of block structures consisting entirely of pure PET sequences that would exhibit melting temperatures similar to the values found for the homopolymer. This point is reconfirmed by the NMR analysis of the copolyesters, which gives no hint to blockiness in these materials. From these results it can be concluded that, under the conditions used for polycondensation, the secondary diol DAS has approximately the same reactivity as ethylene glycol and both monomers will be built in the chain at random.

Certainly the most interesting feature displayed by Figure 3 is the raise of  $T_g$  with an increasing number of DAS moieties built into the chains. The previous study<sup>7</sup> of the homopolyesters composed from DAS and terephthalic acid revealed that these materials have high glass transition temperatures around  $200^\circ\text{C}$ . The present analysis corroborates the finding that the stiff DAS units have the tendency to raise the glass transition markedly. It furthermore shows that the transition points rise linearly with the content of DAS moieties built into the chains. This again is compatible with the notion that we are dealing with random copolymers.

Thus, it has been demonstrated that the glass transition temperature of PET can be raised in a well-defined fashion by partial replacement of glycol units by DAS moieties. Depending on composition, glass transition temperatures well above  $100^\circ\text{C}$  can be reached with  $T_g$  rising linearly with increasing DAS content, rendering DAS an interesting diol component for tailoring the properties of polyesters.

Financial support by the Bundesministerium für Forschung und Technologie, and by the Cerestar GmbH is gratefully acknowledged.

References

1. H. U. Woelk, *Starch/Stärke*, **33**, 397 (1981); and *Nachr. Chem. Technol. Lab.*, **30**, 204 (1982).
2. H. Koch and H. Röper, *Starch/Stärke*, **40**, 121 (1988).
3. M. Eggersdorfer, S. Warwel, and G. Wulff, Eds., *Nachwachsende Rohstoffe*, VCH, Weinheim, 1993.
4. H. Koch and H. Röper, *Starch/Stärke*, **42**, 123 (1990).
5. J. Thiem and H. Lüders, *Starch/Stärke*, **36**, 170 (1984).
6. J. Thiem and H. Lüders, *Polym. Bull.*, **11**, 365 (1984).
7. R. Storbeck, M. Rehahn, and M. Ballauff, *Makromol. Chem.*, **194**, 53 (1993).
8. R. Storbeck and M. Ballauff, *Polymer*, **34**, 5003 (1993).
9. J. Thiem and F. Bachmann, *Makromol. Chem.*, **192**, 2163 (1991).
10. J. Thiem and H. Lüders, *Makromol. Chem.*, **187**, 2775 (1986).
11. J. Feldmann and H. Koebernick, Ger. Pat. 3,041,626; and *Chem. Abstr.*, **97**, 163,414 (1982).
12. J. Feldmann, H. Koebernick, and H. U. Woelk, Ger. Pat. 3,041,673; and *Chem. Abstr.*, **97**, 163,415 (1982).

R. STORBECK  
M. BALLAUFF\*

Polymer-Institut  
Universität (T.H.) Karlsruhe  
Kaiserstrasse 12, 76128 Karlsruhe, Germany

Received December 28, 1994

Accepted July 30, 1995

---

\* To whom correspondence should be addressed.