Polyester Polyols: Synthesis and Characterization of Diethylene Glycol Terephthalate Oligomers

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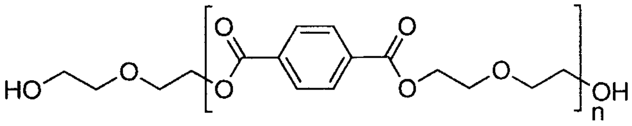
ABSTRACT: The composition of polyester polyols derived from terephthalic acid (TPA) and diethylene glycol (DEG) was examined. The synthesis of individual oligomers **1**,**n** is described. The compounds were characterized with ^{1}H and ^{13}C NMR, mass spectrometry, and elemental analyses. The resonance signals arising from aromatic protons in **1**,**n** = 1–3 were identified in ^{1}H NMR spectra of TPA-DEG condensates. From ^{1}H NMR studies and chromatographic separation, it was concluded that the condensation of TPA and DEG in a 1:2 molar ratio results in a mixture of linear oligomers **1** with the average $\tilde{n}$ varying from 1.1 to 2.2, and containing about 2% of cyclic oligomer **2**. © 2003 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 41: 1114–1123, 2003

Keywords: esterification; oligomers; synthesis; polycondensation

INTRODUCTION

Polyester polyols[1,2] based on aliphatic and aromatic dicarboxylic acids are valuable materials in polymer technologies.[3–5] Among them are low-molecular-weight oligomeric derivatives of phthalic and terephthalic acids that are widely used in high-strength and rigidity polyesters and polyurethane foams.[4,6] The use of aromatic acids offers many advantages to polymer properties including good mechanical characteristics, high thermal stability, resistance to major chemical solvents, and low flammability.

Terephthalate-based polyester polyols are readily prepared by the reaction of terephthalic acid (TPA) with glycols, such as diethylene glycol (DEG), at temperatures above 220 °C.[7] This equilibrium process involves esterification reactions with evolving water, hydrolysis of ester links, and transesterification reactions, and results in a complex mixture of oligomers with a wide range of molecular weights. The principal components in TPA-DEG polyester polyols are oligomers **1**, but cyclic compounds such as **2** may also be present in the polyol mixture. The presence of cyclic polyesters can be anticipated on the basis of findings for other polymers,[8–10] but, without hydroxyl function, they are ineffectual and undesired byproducts.



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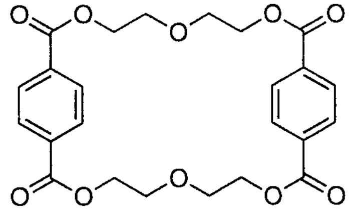

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Large-scale polyurethane foam technological processes require polyols to be liquids at ambient

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Table 1. Statistical Condensation of TPA and DEG in 1:2 Molar Ratio

	Distillation Time (min)			
	Atmospheric	Vacuum (250–300 Torr)	Acid Number (mg KOH/g)	Hydroxyl Number (mg KOH/g)
Run 1	210	120	1.06	231
Run 2[a]	120	30	0.92	197
Run 3[a,b]	150	90	0.42	270

[a] Fifty parts per million of Ti as Tyzor® PC-42 catalyst.
[b] Twenty-centimeter Vigreux column.

temperatures and possess a high hydroxyl content. In the case of TPA-DEG polyols, this is achieved with TPA and DEG in about a 1:2 molar ratio and by targeting the monomer, **1**,**n** = 1. Free DEG remaining in such statistical polyol mixtures acts as a liquidifier and helps to minimize the content of free carboxylic acid that is detrimental to the reaction with isocyanate and foam formation. Despite a number of patents[11,12] and technological processes[13] involving low-molecular-weight TPA-DEG polyols, the properties of individual oligomers **1** and compositions of the polyol mixtures are not known. Also, it is not known whether cyclic polyesters such as **2** are formed in the oligocondensation process and to what extent.

In this work, we prepare the first three oligomers **1**,**n** in the pure form and analyze their physical properties. Subsequently, we investigate the composition of polyol mixtures obtained from TPA and DEG in 1:2 molar ratios under various reaction conditions, with ^{1}H NMR spectroscopy.

RESULTS AND DISCUSSION

Synthesis of Diethylene Glycol Terephthalate Polyester Polyols

Statistical Oligocondensation

Condensation of TPA with DEG in a 1:2 molar ratio was carried out at 225–230 °C. Volatiles were distilled-off under ambient pressure for 3.5 h (run 1 in Table 1). The addition of Tyzor® PC-42 catalyst increased the rate of esterification and shortened the distillation time to about 2 h (runs 2 and 3). At this point the acid number ranged between 15 and 20 mg KOH/g. Further lowering of the acid number was accomplished by distilling-off water from the reaction mixture under reduced pressure (250–300 Torr). This brought the reaction to almost completion and the acid number to about 1 mg KOH/g. The atmospheric pressure distillate contained mostly water (70–90%), and the distillate obtained under reduced pressure contained mostly DEG (90%).

This analysis shows significant differences in the composition of the three mixtures obtained in runs 1–3. ^{1}H NMR spectra of the polyol mixtures showed similar intensities of the signals in the aromatic regions [Fig. 1(a)], whereas in run 2 the low-field signal (8.12 ppm) attributed to **1**,**n** = 1 (*vide infra*) appears less intense. This is consistent with the lower content of DEG that might have been lost from the reaction mixture during the initial vigorous distillation process. The DEG overhead losses were reduced when a short Vigreux column (20 cm, 2–3 theoretical plates) was used. This is reflected in the highest hydroxyl number (270 mg KOH/g) in run 3. Thus, the catalysts appears to significantly reduce the reaction time, whereas the Vigreux column helps to retain DEG in the reaction pot and to achieve the high OH number.

Targeted Synthesis of Oligomers

The preparation of individual oligomers **1** was accomplished with DEG and TPA, both monoprotected with a benzyl group, which was conveniently removed under mild hydrogenation conditions in the final stages of the synthetic sequence. The commercial monobenzyl ether (BDEG) contains about 3% w/w (5 mol %) of unprotected DEG, and for some syntheses it was necessary to purify it by chromatographic methods. The monobenzyl ester **3** was prepared by a stoichiometric reaction of terephthaloyl chloride (**4**) with benzyl alcohol followed by hydrolysis of the unreacted chlorocarbonyl groups (Scheme 1). The acid **3** was

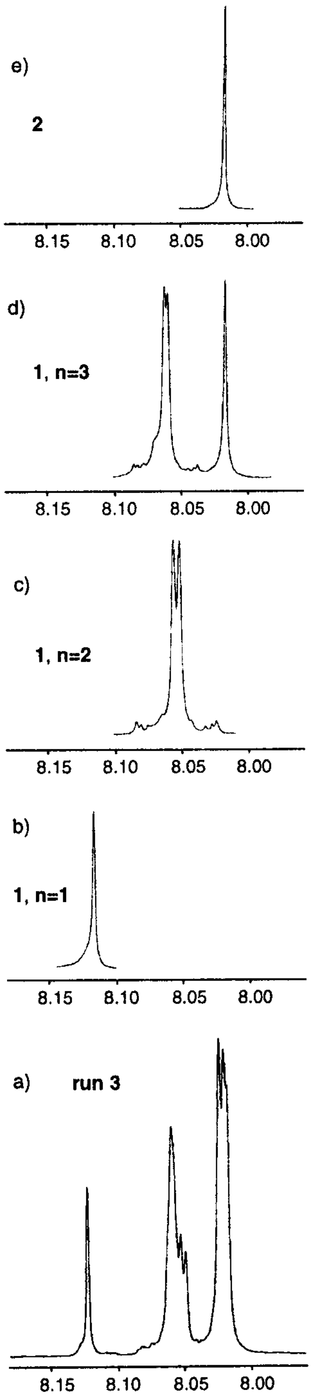
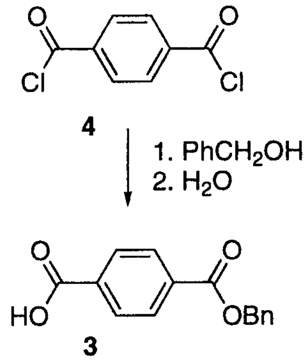


Figure 1. Aromatic portion of ^1H NMR (300 MHz) spectra: (a) reaction mixture in run 3, (b) monomer **1**,**n** = 1, (c) dimer **1**,**n** = 2, (d) trimer **1**,**n** = 3, and (e) cyclic dimer **2**.

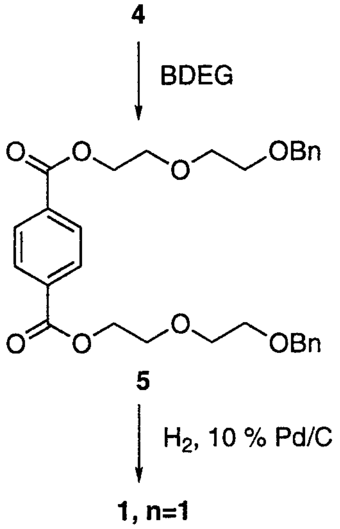
conveniently isolated in 47% overall yield by Soxhlet extraction followed by recrystallization. This method is an attractive alternative to a two-step preparation of **3** from 4-formylbenzoic acid,[14] and represents a significant improvement over the literature methods that involve partial hydrogenation[15,16] or hydrolysis[17] of dibenzyl terephthalate.



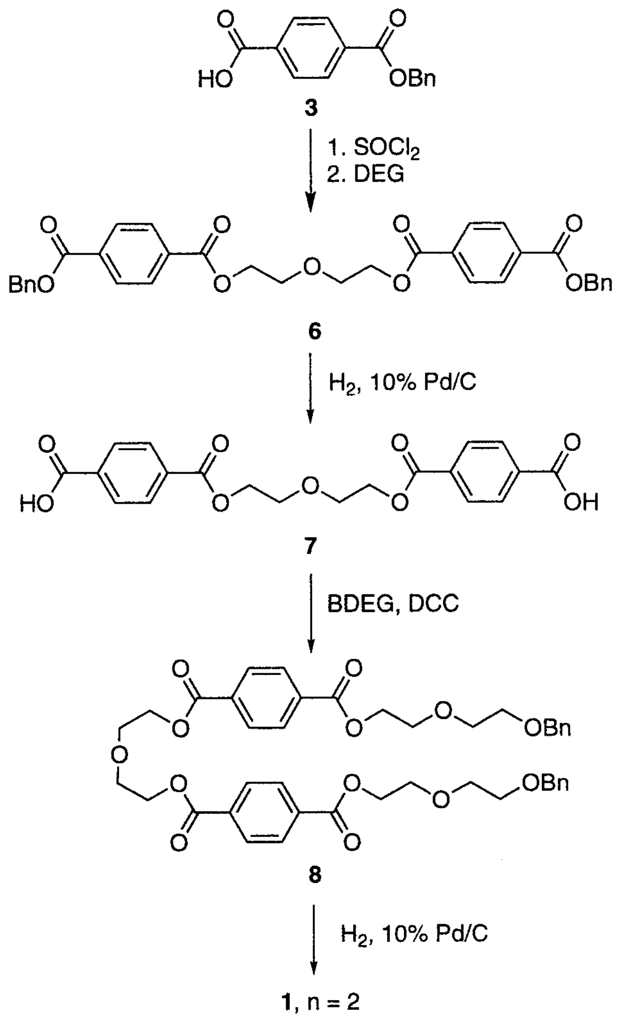
Scheme 1

The synthesis of bis(diethylene glycol) terephthalate (**1**,**n** = 1) is outlined in Scheme 2. The two-step process of alcoholysis of dichloride **4** with BDEG followed by H_2/Pd deprotection of the resulting ester **5** gave 29% overall yield of rigorously purified diol **1**,**n** = 1.

The preparation of two-ring diol **1**,**n** = 2 was accomplished in five steps and 31% overall yield, as shown in Scheme 3. The formation of dibenzyl ester **6** with acid chloride derived from the monoprotected TPA **3** was a high yield and straightforward process. In contrast, the esterification of dicarboxylic acid **7** with BDEG through the corresponding diacid dichloride gave a complex mixture of products. This was presumably due to



Scheme 2



Scheme 3

partial cleavage of the ether linkage in diacid **7** in the reaction with $SOCl_2$. The method of choice was the dicyclohexylcarbodiimide (DCC) assisted esterification, which gave the desired tetraester **8** in 54% yield. When commercial BDEG was used in the reaction, small quantities (ca. 4%) of cyclic esters **2** were identified in the crude product by ^{1}H NMR. The cyclic byproduct, presumably formed from free DEG in the starting BDEG, was difficult to remove from the crude reaction mixture. However, it was easily separated by column chromatography from the polar diol **1,n** = 2 obtained after hydrogenation of the crude tetraester **8**. Pure compound **8** was obtained when diacid **7** was esterified with purified BDEG.

The preparation of three-ring oligomer **1,n** = 3 is outlined in Scheme 4. Thus, DEG terephthalate (**1,n** = 1) was esterified with benzyl TPA **3** to yield hexaester **9**. Subsequent hydrogenolysis removed the benzyl groups in **9** and gave the diacid **10**. Esterification of the diacid with purified BDEG with the DCC method yielded the octaester **11**. Final deprotection gave pure three-ring diol **1,n** = 3 in 12% overall yield on the basis of **1,n** = 1.

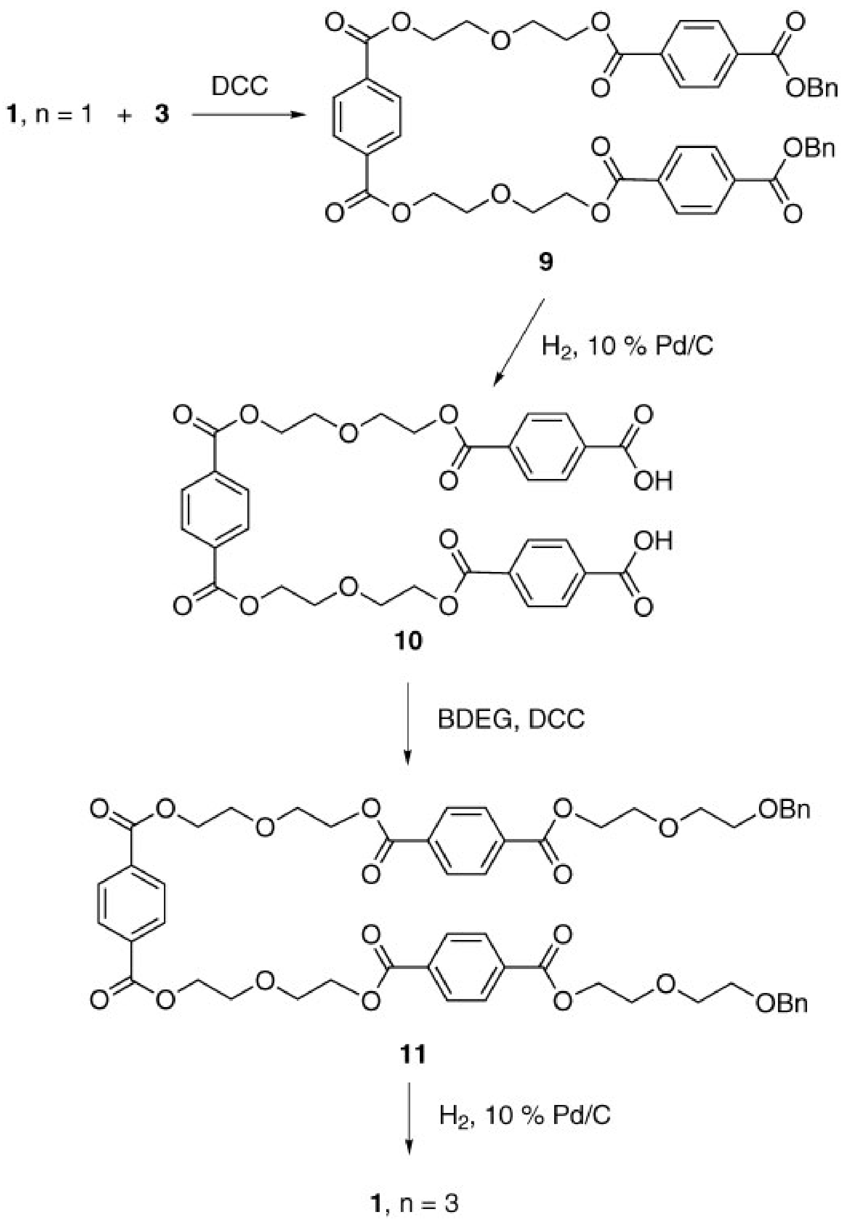
NMR Spectroscopy

^{1}H NMR signals of oligomers **1** are grouped in four distinct regions of the NMR spectrum. The COOC$\underline{\text{H}}_2$— protons are located at about 4.5 ppm, the —C$\underline{\text{H}}_2$—O— protons are in the region of 3.6–3.9 ppm, and the broad OH signal is found at about 2.1 ppm. The methylene group signals generally appear as distorted triplets at ambient temperature[18] and are described as multiplets in the experimental. The most diagnostic are ^{1}H NMR signals of the para-disubstitiuted benzene ring that appear about 8 ppm (Fig. 1). The most downfield shifted is the singlet of **1,n** = 1 at 8.12 ppm [Fig. 1(b)]. The resonance of the terephthaloyl protons is shifted upfield by 0.07 ppm in the dimer **1,n** = 2 [Fig. 1(c)]. In the trimer **1,n** = 3, the ^{1}H signal of the central ring appears at 8.02 ppm [Fig. 1(d)], which coincides with the resonance found in cyclic ester **2** [Fig. 1(e)]. Despite the significant similarities of the ester groups in dimer **1,n** = 2, the ring hydrogen atoms are not chemical-shift equivalent, and the signals appear as a closely spaced (0.02 ppm) AA′BB′ pattern. The same is observed for the peripheral benzene rings in trimer **1,n** = 3.

The differentiation of the terephthaloyl groups is also clearly seen in the ^{13}C NMR spectra of diols **1,n** = 2 and **n** = 3. The ^{13}C=O resonances for the terminal rings in both diols are 0.06 ppm apart, and the resonance of the carbonyl group of the central ring in the trimer is between the two other carbonyl signals. Very similar trends are observed in the ^{1}H NMR and ^{13}C NMR spectra for the benzyl-protected diols.

Thermal Analysis

The melting points for the three diols **1** are above 50 °C. This is consistent with the observed slow solidification upon standing of the TPA-DEG statistical polyol mixture (1:2 ratio). The first two oligomers have similar melting points at about 53 °C, whereas the trimer **1,n** = 3 melts above 70 °C. Thermal analysis of diols **1** indicates that the enthalpy of melting is generally around 0.12 kJ/g for the first two oligomers and slightly lower (0.10



Scheme 4

kJ/g) for **1**,**n** = 3. The results are summarized in Table 2.

The cyclic tetraester **2** exhibits a broad melting behavior above 200 °C that appears to be sample dependent. Compound **2** isolated from run 3 melted in the range of 212–214 °C, in contrast with the literature reports ranging from 200–20[19] to 220–230 °C.[8] This is presumably due to a ring-opening polymerization of **2** catalyzed by small impurities present in the sample. Support for this is provided by differential scanning calorimetry (DSC) analysis that shows a broad exotherm with

Table 2. Thermal Analysis of Oligomeric Diols **1**[a]

Compound	Onset (°C)	Enthalpy of Melting (kJ/mol)	Enthalpy of Melting (kJ/g)
1, **n** = 1	50.2	40.4	0.12
1, **n** = 2	50.3	69.1	0.12
1, **n** = 3	69.3	80.6	0.10

[a] Heating rate: 4 °C/min.

Table 3. Chromatographic Separation of Run 3 Crude Mixture (10.000 g)

Fraction	Eluant	Yield (g)	Main Product As Identified by ^{1}H NMR
1	CH_2Cl_2/Et_2O (1:1)	0.173	**2**
2	CH_2Cl_2/Et_2O (1:1)	0.065	Aldehydic byproducts
3	CH_2Cl_2/Et_2O (1:1)	5.372	**1**, **n** = 1–3 and higher, $\tilde{n}$ = 1.7–1.8
4	EtOAc	0.620	**1**, **n** = 1–3
5	Acetone	2.860	**1**, **n** = 1–3 and DEG
6	EtOH	0.817	DEG
Total		9.907	

the maximum at 202 °C and ΔH = 83 J/g before melting of **2** at 216 °C (onset) and ΔH = 92 J/g.

Composition of TPA-DEG Oligomeric Mixtures

^{1}H NMR analysis demonstrated that all three oligomers **1**,**n** are present in the reaction mixtures resulting from polycondensation reactions in runs 1–3 (Table 1). The aromatic portion of the ^{1}H NMR spectrum of the mixture from run 3 is displayed in Figure 1(a). The most downfield signal at 8.12 ppm can be ascribed to monomer **1**,**n** = 1. The group of signals at about 8.06 ppm corresponds to the outer benzene rings, whereas the multiplet at about 8.02 ppm indicates the presence of inner benzene rings in the oligomeric strand of **1**,**n**. With the exception of the AA′BB′ system of dimer **1**,**n** = 2 appearing as a high-field shoulder doublet feature in the 8.06 ppm multiplet, it is difficult to assign the remaining peaks in the 8.06 and 8.02 ppm multiplets. It is certain, however, that trimer **1**,**n** = 3 and higher oligomers are present in the mixture. Protons of the inner benzene rings in the trimer and higher oligomers are partially overlapped with each other as well as with aromatic protons of cyclic polyester **2**. Thus, ^{1}H NMR does not allow determination of the distribution of oligomers in the mixture quantitatively because of significant signal overlap, and only the ratio of monomer **1**,**n** = 1 to the total amount of oligomers **1** can be determined. The NMR spectrum also does not allow a reliable estimate of the amount of the cyclic isomer **2** formed in the statistical oligocondensation process. To assess the yield of **2**, a polyester polyol mixture from run 3 was fractionated by column chromatography, and the results are listed in Table 3. The cyclic tetraester **2** was isolated in less than 2% yield, which is consistent with other reports on the content of cyclic esters in polyesters.[8–10] This indicates that the cyclization is a minor process during the TPA-DEG condensation reaction, and a small high-field shoulder signal in the 8.02 ppm multiplet in the ^{1}H NMR spectrum of the polyol mixture can be attributed to **2**.

Analysis of the NMR spectra yields the value of average degree of oligomerization $\tilde{n}$ as a ratio of intensity of all aromatic proton signals to the intensity of $C\underline{H}_2OH$ signals at 3.75 ppm (Table 4). The average degree of oligomerization $\tilde{n}$ obtained from the NMR data is very close to the value calculated from the experimental hydroxyl number #OH values of polyols with eq 1

$$\tilde{n} = [112{,}220 - 106.12 \times (\#OH)]/[236.22 \times (\#OH)] \quad (1)$$

The first number in eq 1 corresponds to the weight of 2 mol of KOH expressed in milligrams

Table 4. Degree of Oligomerization in Polyester Polyols Derived from TPA and DEG in a Molar Ratio 2:1

		Average Degree of Oligomerization $\tilde{n}$	
Experiment	Fraction of **1**, **n** = 1[a]	From ^{1}H NMR[b]	From #OH[c]
Run 1	0.14	1.6	1.6
Run 2	0.09	2.2	2.0
Run 3	0.21	1.1	1.3

[a] Ratio of ^{1}H NMR aromatic signal intensity for **1**, **n** = 1 at 8.12 ppm to all aromatic protons.

[b] Ratio of all aromatic signals to $\underline{CH_2}OH$ signals at 3.75 ppm.

[c] From eq 1.

per mole, the second value is the molar weight of the terminal DEG chain, and the third number is the molecular weight of the repeating unit in **1**,**n**.

The lowest degree of oligomerization is observed in run 3 in which the losses of DEG were minimized with a Vigreux column, and the highest in run 2 was presumably due to the initial vigorous boil-off and loss of DEG. The values of $\tilde{n}$ obtained in both methods agree with the concentration of monomer **1**,**n** = 1 in the mixture.

EXPERIMENTAL

Melting points were measured by the capillary method. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a DRX-300 Bruker instrument with tetramethylsilane as the internal standard, unless stated otherwise. Elemental analyses were performed by Atlantic Microlab (Norcross, GA). Mass spectra were obtained at the Mass Spectrometry Facility of Notre Dame University in a nitrobenzyl alcohol (NBA) matrix with the positive fast atom bombardment (FAB+) method for ion generation. DSC analysis was done on a TA 2920 instrument with the scanning rate of 4 °C/min. Silica gel 60 (230–400 mesh) was used for liquid column chromatography. Yields are given for pure products after several recrystallizations.

Acid numbers #H for polyester polyols, defined as the amount of potassium hydroxide required to neutralize 1.00 g of polyol, were measured according to the ASTM D 4662-98 procedure. Hydroxyl numbers #OH, defined as the amount of potassium hydroxide equivalent to the amount of acetic acid involved in the esterification reaction with 1.00 g of polyol, were determined with the acetic anhydride method described in the ASTM E 222 procedure.

TPA, DEG, and titanate esterification catalyst Tyzor® PC-42 were provided by DuPont (more information about the catalyst is available at www.dupont.com/tyzor). Terephthaloyl chloride **4** and BDEG were purchased from Aldrich and used as received. For the preparation of **11**, BDEG was purified by column chromatography that removed the residual DEG showing up in the range of 3.54–3.57 ppm in the ^{1}H NMR spectrum.

General Procedure for Synthesis of Polyester Polyols (Runs 1–3)

A mixture of TPA and DEG in a molar ratio of 1:2 (a typical load: 800–900 g) were stirred at 225–230 °C in a 1-L three-necked flask equipped with a mechanical stirrer, thermometer, and a distillation head. After the rate of distillation significantly decreased and the mixture became clear, the distillation was continued under reduced pressure (250–300 Torr) until a low acid number was obtained. In runs 2 and 3, 0.72 g of Tyzor® PC-42 catalyst (50 ppm of Ti) was added to the reaction mixture. In run 3 a 20-cm Vigreux column was used. Reaction times and results are given in Table 1.

Bis(1-hydroxy-3-oxapentyl) Terephthalate (1,n = 1)

A 10% Pd on charcoal (3.338 g) in absolute ethanol (EtOH, 25 mL) was placed in a hydrogenation apparatus, saturated with hydrogen under a pressure of 5 atm, and evacuated. The saturation/evacuation cycle was repeated three times. Hydrogen was evacuated again, and a solution of compound **5** (5.837 g, 0.011 mol) in dry benzene (25 mL) was added to the activated catalyst at atmospheric pressure. With the same evacuating and filling procedures, the hydrogen pressure in a reactor was established at the level of 5 atm, and the reaction mixture was shaken for 4 h. The reaction mixture was filtered, the filter was washed three times with benzene (10–15 mL), and the filtrate was evaporated to dryness. The resulting residue was chromatographed on a silica gel column with CH_2Cl_2 to elute traces of starting material, and subsequently ethyl acetate (EtOAc) to elute the product. The eluate was evaporated to dryness. The oily residue was crystallized from EtOH, and then it was recrystallized twice from the same solvent to give 2.143 g (56% yield) of **1**,**n** = 1; mp: 53–55 °C.

^{1}H NMR (δ): 2.06 (br, 1H), 3.64–3.67 (m, 2H), 3.72–3.77 (m, 2H), 3.84–3.87 (m, 2H), 4.51–4.53 (m, 2H), 8.12 (s, 2H). ^{13}C NMR (δ): 61.74, 64.39, 69.07, 72.42, 129.64, 133.88, 165.72. FAB mass spectrometry (MS) (*m/z*): 343 (61, $[M+H]^+$), 281 (76, $[M\text{-}HOCH_2CH_2O]^+$), 237 (100, $[M\text{-}HOCH_2CH_2\text{-}OCH_2CH_2O]^+$). ELEM. ANAL. Calcd. for $C_{16}H_{22}O_8$: C, 56.14%; H, 6.48%. Found: C, 56.34%; H, 6.52%.

1,5-Bis[(1-hydroxy-3-oxapentyloxy)terephthalyloxy]-3-oxapentane (1,n = 2)

Diol **1**,**n** = 2 was obtained by hydrogenolysis of dibenzyl derivative **8** (0.956 g, 1.26 mmol) as described above for the preparation of **1**,**n** = 1. The product was eluted with an EtOAc/acetone mixture (5:1 ratio). Yield: 0.581 g (80%) of white powder; mp: 52.5–53.5 °C.

^{1}H NMR (δ): 2.40 (br, 1H), 3.64–3.67 (m, 2H), 3.74–3.77 (m, 2H), 3.84–3.91 (m, 4H), 4.50–4.54 (m, 4H), 8.04 and 8.06 (AB, 4H). ^{13}C NMR (δ): 61.73, 64.21, 64.40, 68.99, 69.06, 72.47, 129.57, 133.78, 133.80, 165.62, 165.68. FAB MS (*m/z*): 579 (20, [M+H]$^+$), 517 (29, [M-HOCH$_2$CH$_2$O]$^+$), 473 (81, [M-HOCH$_2$CH$_2$OCH$_2$CH$_2$O]$^+$). ELEM. ANAL. Calcd. for $C_{28}H_{34}O_{13}$: C, 58.13%; H, 5.92%. Found: C, 58.15%; H, 5.82%.

Bis{1-[(1-hydroxy-3-oxapentyloxy)terephthalyloxy]-3-oxapentyloxy} Terephthalate (1,n = 3)

Hydrogenolysis of compound **11** (0.291 g, 0.29 mmol) in the same manner as described for **1,n** = 1 gave 0.086 g (36% yield) of pure **1,n** = 3 after recrystallization from EtOH; mp: 73–74 °C.

^{1}H NMR (400 MHz) δ: 2.13 (br, 1H), 3.65–3.67 (m, 2H), 3.74–3.77 (m, 2H), 3.84–3.87 (m, 2H), 3.89–3.91 (m, 4H), 4.50–4.54 (m, 6H), 8.02 (s, 2H), 8.04–8.09 (m, 4H). ^{13}C NMR (δ): 61.74, 64.27, 64.40, 69.03, 69.07, 72.43, 129.55, 129.58, 133.76, 133.81, 165.62, 165.64, 165.68. FAB MS (*m/z*): 815 (8, [M+H]$^+$), 753 (12, [M-HOCH$_2$CH$_2$O]$^+$), 709 (23, [M-HOCH$_2$CH$_2$OCH$_2$CH$_2$O]$^+$). ELEM. ANAL. Calcd. for $C_{40}H_{46}O_{18}$: C, 58.96%; H, 5.69%. Found: C, 58.52%; H, 5.67%.

3,6,9,16,19,22-Hexaoxatricyclo[22.2.2.2^{11,14}]-triaconta-1(27),11(30), 12,14(29),24(28),25-hexaene-2,10,15,23-tetraone (2)

The product was isolated from 10 g of the polyol mixture obtained in run 3 with silica gel column chromatography (CH$_2$Cl$_2$/Et$_2$O mixture in a 1:1 ratio) followed by recrystallization from EtOH; mp: 212–214 °C (lit.[20] 214 °C; lit.[19] 200–204 °C; lit.[8] 220–223 °C).

^{1}H NMR (δ): 3.86–3.88 (m, 4H), 4.54–4.56 (m, 4H), 8.02 (s, 4H) (lit.[21] δ 3.88, 4.57, 8.05). ^{13}C NMR (δ): 63.76, 68.67, 129.50, 133.91, 165.61 (lit.[21] δ 64, 78.5, 119.5, 134, 166). MS (*m/z*): 473 (12, [M+H]$^+$), 429 (4, [M—CH$_2$CH$_2$O+H]$^+$). ELEM. ANAL. Calcd. for $C_{24}H_{24}O_{10}$: C, 61.01%; H, 5.12%. Found: C, 60.82%; H, 5.14%.

Monobenzyl Terephthalate (3)

A solution of benzyl alcohol (35.0 g, 0.323 mol) in pyridine (50 mL) was added dropwise for 2 h to a stirred solution of terephthaloyl dichloride (**4**, 65.0 g, 0.323 mol) in pyridine (200 mL) under reflux. The reflux was continued for 2 h more, and then the mixture was poured into 1 L of cold water. The white precipitate was filtered, washed with 3 L of cold water, and dried. The resulting solid was extracted with CH$_2$Cl$_2$ in a Soxhlet extraction apparatus for 48 h. The extract was evaporated to dryness, and the solid residue was recrystallized three times from a EtOH/chloroform (CHCl$_3$) mixture (1:1 ratio). Yield: 39.2 g (47%) of needlelike crystals; mp: 178–180 °C (lit.[16] 181 °C; lit.[14] 178–179 °C).

^{1}H NMR (δ, acetone-*d*$_6$): 5.42 (s, 2H), 7.35–7.45 (m, 3H), 7.52–7.54 (m, 2H), 8.17 (s, 4H). ELEM. ANAL. Calcd. for $C_{22}H_{18}O_4$: C, 70.31%; H, 4.72%. Found: C, 70.27%; H, 4.69%.

Bis(1-benzyloxy-3-oxapentyl) Terephthalate (5)

DEG benzyl ether (15.01 g, 0.076 mol) in toluene (20 mL) was added dropwise to a stirred solution of terephthaloyl dichloride (**4**, 7.76 g, 0.038 mol) in a mixture of toluene and pyridine in a 1:1 ratio (40 mL). The reaction mixture was stirred and refluxed for 6 h. The precipitate of pyridinium chloride was filtered off, and solvents were removed under reduced pressure. The residue was dissolved in diethyl ether, and the solution was washed four times with water. The organic layer was dried (MgSO$_4$) and evaporated to dryness. The product was purified on a silica gel column (CH$_2$Cl$_2$) and recrystallized twice from EtOH to give 10.11 g (51% yield) of white crystals; mp: 50–50.5 °C.

^{1}H NMR (δ): 3.64–3.67 (m, 2H), 3.72–3.75 (m, 2H), 3.84–3.87 (m, 2H), 4.49–4.53 (m, 2H), 4.57 (s, 2H), 7.23–7.33 (m, 5H), 8.09 (s, 2H). ELEM. ANAL. Calcd. for $C_{30}H_{34}O_8$: C, 68.95%; H, 6.56%. Found: C, 69.10%; H, 6.56%.

1,5-Bis(benzyloxyterephthalyloxy)-3-oxapentane (6)

A mixture of monobenzyl terephthalate (**3**, 5.575 g, 21.75 mmol) and thionyl chloride (50 mL) was stirred at reflux for 30 min. Excess SOCl$_2$ was distilled-off under an aspirator vacuum, and the oily residue was dried in vacuum (2 Torr). The resulting acid chloride was added to a solution of DEG (1.154 g, 10.88 mmol) in a mixture of pyridine/toluene in a 1:1 ratio (75 mL). The reaction mixture was protected from atmospheric moisture with a CaCl$_2$ tube and stirred for 12 h at 90 °C. The solvents were evaporated, and the residue was extracted with EtOAc (100 mL). The extract was washed with water (3 × 25 mL), dried

($MgSO_4$), and evaporated to dryness. The residue was recrystallized twice from EtOH to give 5.985 g (94% yield) of a white powder; mp: 90–93 °C.

^{1}H NMR (δ, acetone-d_6): 3.91–3.94 (m, 2H), 4.49–4.52 (m, 2H), 5.40 (s, 2H), 7.35–7.44 (m, 3H), 7.51–7.53 (m, 2H), 8.07 (s, 4H). ^{13}C NMR (δ): 64.29, 67.13, 69.07, 128.28, 128.41, 128.66, 129.63, 133.79, 134.00, 135.68, 165.53, 165.67. ELEM. ANAL. Calcd. for $C_{34}H_{30}O_9$: C, 70.09%; H, 5.19%. Found: C, 70.30%; H, 5.10%.

1,5-Bis(4-carboxybenzoyloxy)-3-oxapentane (7)

Compound **6** was debenzylated in a manner as described above for **1**,**n** = 1. Increased amounts of solvents and catalyst were used in this case as the reaction product has low solubility. Dibenzyl derivative **6** (1.997 g, 3.43 mmol) was dissolved in a mixture of toluene/absolute EtOH (2:1 ratio, 150 mL) and added to 1.371 g of activated 10% Pd/C in absolute EtOH (50 mL). Without chromatographic purification, solid crude product was recrystallized twice from EtOH to give 1.058 g (77% yield) of the white powdery product. In another synthesis from 2.067 g of **6**, the yield of **7** was 0.828 g (58%); mp: 207–211 °C (dec).

^{1}H NMR (δ, acetone-d_6): 3.93–3.96 (m, 2H), 4.50–4.54 (m, 2H), 8.10 (s, 4H). ^{13}C NMR (δ, acetone-d_6): 65.03, 65.91, 130.24, 130.49, 134.84, 135.31, 165.90, 166.63. FAB MS (*m/z*): 403 ($[M+H]^+$). ELEM. ANAL. Calcd. for $C_{20}H_{18}O_9$: C, 59.70%; H, 4.51%. Found: C, 59.55%; H, 4.53%.

1,5-Bis[(1-benzyloxy-3-oxapentyloxy)-terephthalyloxy]-3-oxapentane (8)

DCC (1.892 g, 9.17 mmol) was added portionwise to a stirred solution of dicarboxylic acid (**7**, 1.538 g, 3.82 mmol), BDEG (1.500 g, 7.65 mmol), and 4-dimethylaminopyridine (0.112 g, 0.92 mmol) in CH_2Cl_2 (50 mL) at 0 °C. The temperature was allowed to rise to ambient, and the reaction mixture was stirred for 24 h. A precipitate of urea was filtered-off, and the filtrate was concentrated by evaporating CH_2Cl_2. A precipitated urea was filtered-off again, and the filtrate was evaporated to dryness. The resulting yellow oil was chromatographed on a SiO_2 column (CH_2Cl_2) to give a yellow oil. The oil was treated with cold acetone, and a white precipitate (40 mg, 4% yield) of pure cyclic ester **2** was separated. The solution was evaporated, and the resulting crude tetraester **8** (0.956 g) was used in the next step without further purification.

Analytical samples of compound **8** were obtained in analogous synthesis with purified BDEG. The yellow oil obtained after chromatography was crystallized and subsequently recrystallized twice from EtOH to give 0.486 g (54% yield) of white powdery product; mp: 38.5–40 °C.

^{1}H NMR (δ): 3.63–3.67 (m, 2H), 3.71–3.75 (m, 2H), 3.84–3.91 (m, 4H), 4.49–4.54 (m, 4H), 4.56 (s, 2H), 7.23–7.33 (m, 5H), 8.07 (s, 4H). ELEM. ANAL. Calcd. for $C_{42}H_{46}O_{13}$: C, 66.48%; H, 6.11%. Found: C, 66.71%; H, 6.54%.

Bis(1-benzyloxyterephthalyloxy-3-oxapentyl) Terephthalate (9)

Compound **9** was synthesized by DCC-assisted esterification of **1** (0.833 g, 2.43 mmol) with monobenzyl terephthalate (**3**, 1.248 g, 4.87 mmol) as described above for **8**. The reaction time was increased to 40 h. The crude product was recrystallized from a $CHCl_3$/EtOH mixture (1:2 ratio) to give 1.635 g (82% yield) of a white powder; mp: 100–103 °C.

^{1}H NMR (δ): 3.87–3.90 (m, 4H), 4.48–4.54 (m, 4H), 5.38 (s, 2H), 7.35–7.46 (m, 5H), 8.02 (s, 2H), 8.07 (s, 2H). ^{13}C NMR (δ): 64.27, 67.12, 69.05, 128.26, 128.40, 128.65, 129.56, 129.61, 133.79, 133.97, 135.67, 165.53, 165.60, 165.66. ELEM. ANAL. Calcd. for $C_{46}H_{42}O_{14}$: C, 67.48%; H, 5.17%. Found: C, 67.38%; H, 5.14%.

Bis[1-(4-carboxybenzoyl)oxy-3-oxapentyl] Terephthalate (10)

Compound **9** (1.421 g, 1.74 mmol) was hydrogenated under the same conditions as described for the synthesis of **7**. Crude product was recrystallized twice from EtOH to give 0.815 g (74% yield) of the diacid; mp: 160–162 °C.

^{1}H NMR (δ, acetone-d_6): 3.93–3.97 (m, 4H), 4.50–4.54 (m, 4H), 8.01 (s, 2H), 8.04 and 8.07 (AB, 4H). FAB MS (*m/z*): 639 $[M+H]^+$. ELEM. ANAL. Calcd. for $C_{32}H_{30}O_{14}$: C, 60.19%; H, 4.74%. Found: C, 60.07%; H, 4.79%.

Bis{1-[(1-benzyloxy-3-oxapentyloxy)terephthalyloxy]-3-oxapentyloxy} Terephthalate (11)

Dicarboxylic acid (**10**, 0.683 g, 1.07 mmol) was esterified with purified BDEG (0.420 g, 2.14 mmol) as described for **8**. The product was purified with column chromatography (silica gel, CH_2Cl_2/EtOAc, 5:1 ratio). Attempts to crystallize the product from various solvents were unsuccessful. The colorless oil obtained after evaporating the eluate crystallized after several days. Yield: 0.602 g (57%); mp: 44 °C.

^{1}H NMR (δ): 3.64–3.67 (m, 2H), 3.72–3.75 (m, 2H), 3.84–3.91 (m, 6H), 4.50–4.54 (m, 6H), 4.57 (s, 2H), 7.26–7.33 (m, 5H), 8.04 (s, 2H), 8.06 (br, 4H). ^{13}C NMR (δ): 64.27, 64.52, 69.05, 69.09, 69.42, 70.74, 73.27, 127.61, 127.68, 128.35, 129.56, 129.61, 133.72, 133.78, 133.95, 138.12, 165.59, 165.67. ELEM. ANAL. Calcd. for $C_{54}H_{58}O_{18}$: C, 65.18%; H, 5.88%. Found: C, 64.89%; H, 5.90%.

CONCLUSIONS

Condensation of TPA and DEG in a 1:2 molar ratio leads to a mixture of linear polyester polyol oligomers **1**,**n** as the major components and negligible amounts (ca. 2%) of cyclic polyester **2**. The average degree of oligomerization varies from 1.1–2.2 depending on the condensation conditions and use of fractionation of the distillate. The first three and presumably all TPA-DEG oligomers are solids melting above 50 °C. NMR spectroscopy does not allow the assessment of the ratio of each oligomer in the polyol mixture but offers a reliable estimate of the average degree of polymerization consistent with that found through analysis of the hydroxyl number.

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