

# Synthesis and Characterization of Oligoethylene Bibenzoate With Hydroxyethyl End Groups

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## SYNOPSIS

In the process of exploring the potential advantage of 4,4'-biphenyl dicarboxylic acid (BDA) as a comonomer in poly(ethylene terephthalate) (PET), it was found that BDA needs to be derivatized for effective incorporation in PET specifically if high levels of BDA incorporation are desired. Bis-hydroxyethylbenzoate (HEB) was synthesized with the anticipation that it would be compatible with both the continuous PET process which uses high-purity terephthalic acid as well as the batch PET process which utilizes dimethyl terephthalate. This article describes the synthesis of HEB and some of the oligoethylene benzoates produced in the process. Diethylene glycol is produced as an undesirable by-product during the reaction. In an effort to produce a minimum amount of diethylene glycol, a catalytic process was investigated which resulted in diethylene glycol levels of less than 0.5%. Quantitative analysis of diethylene glycol, performed by gas chromatography, and the oligomer structure studies performed by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR are described. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

4,4'-Biphenyl dicarboxylic acid (BDA) was polymerized with both the aliphatic<sup>1-5</sup> and aromatic diols.<sup>6</sup> Wholly aromatic polyesters based on BDA are generally very rigid and so comonomers with lateral substitution or a kink have been used to lower the melting point and, hence, the processing temperature.<sup>6</sup> Polyesters of BDA with long-chain aliphatic diols form highly ordered thermotropic smectic mesophases<sup>2,5</sup>; polyesters with short-chain diol, poly(ethylene benzoate) (PEB), e.g., melt to an anisotropic phase very close to the decomposition temperature which makes it difficult to identify the exact nature of the mesophase.<sup>2</sup> For preparing a thermally processable polymer from BDA and ethylene glycol, the melting temperature of the polymer will need to be reduced. The crystallinity and therefore the melting behavior of PEB is modified by copolymerization with other diacids or diols. Copolymers of PEB with poly(butylene benzoate) are found to melt to the anisotropic phase and give

an excellent balance of strength and toughness.<sup>7</sup> BDA has been used to improve the  $T_g$  and physico-mechanical properties of poly(ethylene terephthalate) (PET).<sup>1</sup> Most of the work published to date utilizes the dimethylbenzoate in a melt polycondensation process to produce polyesters. However, for modifying the properties of PET, there is a desire to utilize the comonomer in the acid form since the continuous PET process is now based on high-purity terephthalic acid and not on dimethyl terephthalate. BDA could be used as a comonomer in the continuous PET process without any need for derivatization if the BDA concentrations were low. Copolymers of BDA and terephthalic acid with higher levels of BDA could not be made conveniently due to the high insolubility and intractability of BDA. This article describes the synthesis and characterization of bis-hydroxyethylbenzoate (HEB) and oligoethylene benzoates which could be used in the PET processes based either on terephthalic acid or dimethyl terephthalate.

During the synthesis of PET, diethylene glycol is produced as a byproduct due to the undesirable dimerization of ethylene glycol.<sup>8-9</sup> Considerable effort is taken to reduce the amount of diethylene glycol because once it is produced it gets incorporated

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## BDA REACTIONS with CATALYSTS

### Reaction Time and DEG Level

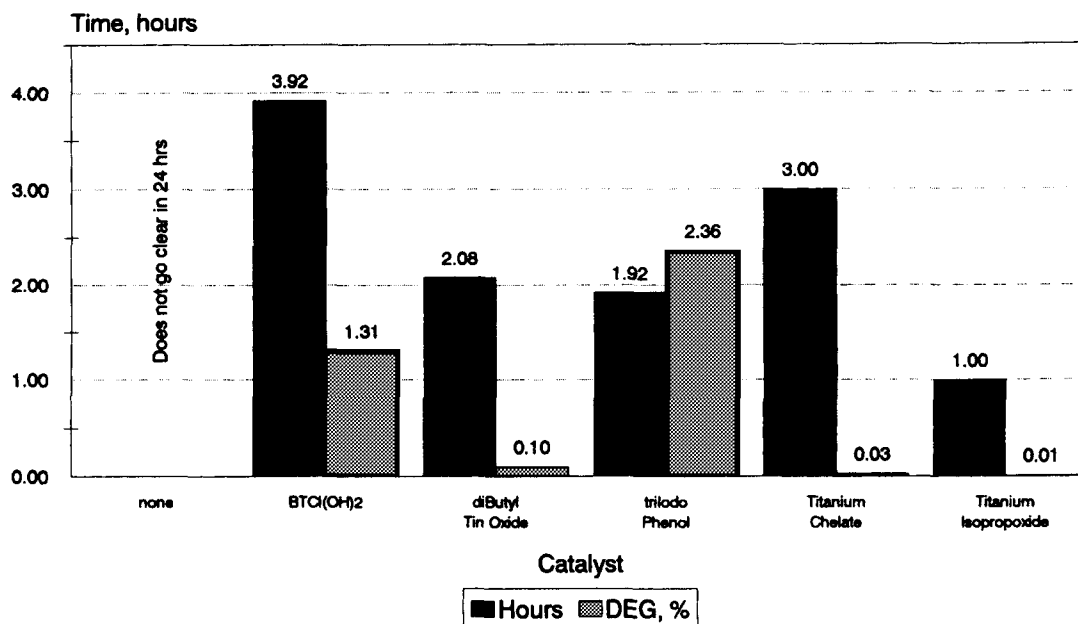


Figure 1 Effect of the catalyst on the reaction time and diethylene glycol formation.

perature for approximately 1–6 h, depending upon the catalyst, with water being removed. When the reaction was complete, the solution turned clear; it was then allowed to cool to approximately ambient temperature. The product was analyzed to determine the presence of any diethylene glycol. The results are shown in Table I.

#### Diethylene Glycol Analysis by GC

Polyester, 1.5–2.0 g, were weighed with analytical accuracy and transferred into a reaction tube. Methanol, 30 mL, containing 24 mg tetramethylene glycol dimethyl ether (internal standard) and 1.8 mg zinc acetate (transesterification catalyst) was pipetted into the reaction tube. The reaction tube was sealed and placed in an appropriate heating block or an oven which had been heated to 220°C. After 3 h, the reaction tube was removed from the heating source and allowed to cool to ambient temperature. The sample was evaluated on a capillary GC column equipped with a flame ionization detector.

#### NMR Instrumentation

Spectra were acquired with Varian (Palo Alto, CA) VXR400 and Varian Unity 400 Fourier transform spectrometers operating at 400 and 100 MHz nominal <sup>1</sup>H and <sup>13</sup>C frequency, respectively. The spectrometers were equipped with a Sun Microsystems (Mountain View, CA) Sparc + 1 computer with 16

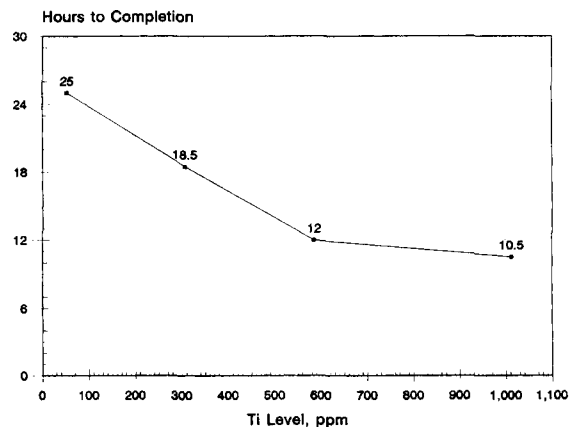


Figure 2 Catalyst level vs. reaction time for HEB.

Table II Peak Assignments

I	II	III	IV	V
<i>C</i>	3.88	60.5	60.6	—COO—CH <sub>2</sub> — <b>CH<sub>2</sub></b> —OH
<i>x</i> <sub>1</sub>	3.62	61.8	61.8	—COO—CH <sub>2</sub> —CH <sub>2</sub> —O—CH <sub>2</sub> — <b>CH<sub>2</sub></b> —OH, HO— <b>CH<sub>2</sub></b> —CH <sub>2</sub> —O—CH <sub>2</sub> — <b>CH<sub>2</sub></b> —OH
<i>A</i>	4.76	63.9	63.7	—COO— <b>CH<sub>2</sub></b> — <b>CH<sub>2</sub></b> —OOC—
<i>X</i>	3.55	64.2	64.2	HO—CH <sub>2</sub> —CH <sub>2</sub> —OH
<i>b</i> <sub>1</sub>	4.52	65.2	64.8	—COO— <b>CH<sub>2</sub></b> —CH <sub>2</sub> —O—CH <sub>2</sub> — <b>CH<sub>2</sub></b> —COO—,
<i>b</i> <sub>2</sub>	4.48	65.4	65.0	—COO— <b>CH<sub>2</sub></b> —CH <sub>2</sub> —O—CH <sub>2</sub> —CH <sub>2</sub> —OH
<i>B</i>	4.41	67.9	67.5	—COO— <b>CH<sub>2</sub></b> —CH <sub>2</sub> —OH
<i>c</i> <sub>1</sub> , <i>c</i> <sub>2</sub>	3.94 3.85	69.4	69.5	—COO—CH <sub>2</sub> — <b>CH<sub>2</sub></b> —O—CH <sub>2</sub> —CH <sub>2</sub> —OH, —COO—CH <sub>2</sub> — <b>CH<sub>2</sub></b> —O—CH <sub>2</sub> —CH <sub>2</sub> — OOC—
Triethylene glycol		71.1		—O—(CH <sub>2</sub> ) <sub>2</sub> —O— <b>CH<sub>2</sub></b> — <b>CH<sub>2</sub></b> —O(CH <sub>2</sub> ) <sub>2</sub> —O—
<i>X</i> <sub>3</sub>	3.60	73.4	73.4	HO—CH <sub>2</sub> — <b>CH<sub>2</sub></b> —O—CH <sub>2</sub> —CH <sub>2</sub> —OH,
<i>X</i> <sub>2</sub>	3.52	73.5	73.5	—COO—CH <sub>2</sub> —CH <sub>2</sub> —O— <b>CH<sub>2</sub></b> —CH <sub>2</sub> —OH

I, Label of carbon and directly bonded proton. Capital letters for major peaks (e.g., monomers); lower-case letters for minor peaks (e.g., dimers). II. <sup>1</sup>H chemical shifts (ppm). III. <sup>13</sup>C chemical shifts (ppm) of terephthalic acid-based reaction product, in ascending order. IV. <sup>13</sup>C chemical shifts of BDA-based reaction product. V. Identification of methylene types (bold-faced).

Mbyte memory and a 700 Mbyte disk, operating on Varian VNMR software, Version 3.2a, and Sun Microsystems SunOS 4.0.3 software. The *T*<sub>1</sub>'s of the methylene carbons were estimated from an inversion recovery experiment. Based on this result, 1-dimensional <sup>13</sup>C spectra earmarked for quantitative evaluation were acquired with a 10.676 s delay between pulses, which is more than five times the longest *T*<sub>1</sub> of all but the <sup>13</sup>C nuclei nearest the chain ends.

## RESULTS AND DISCUSSION

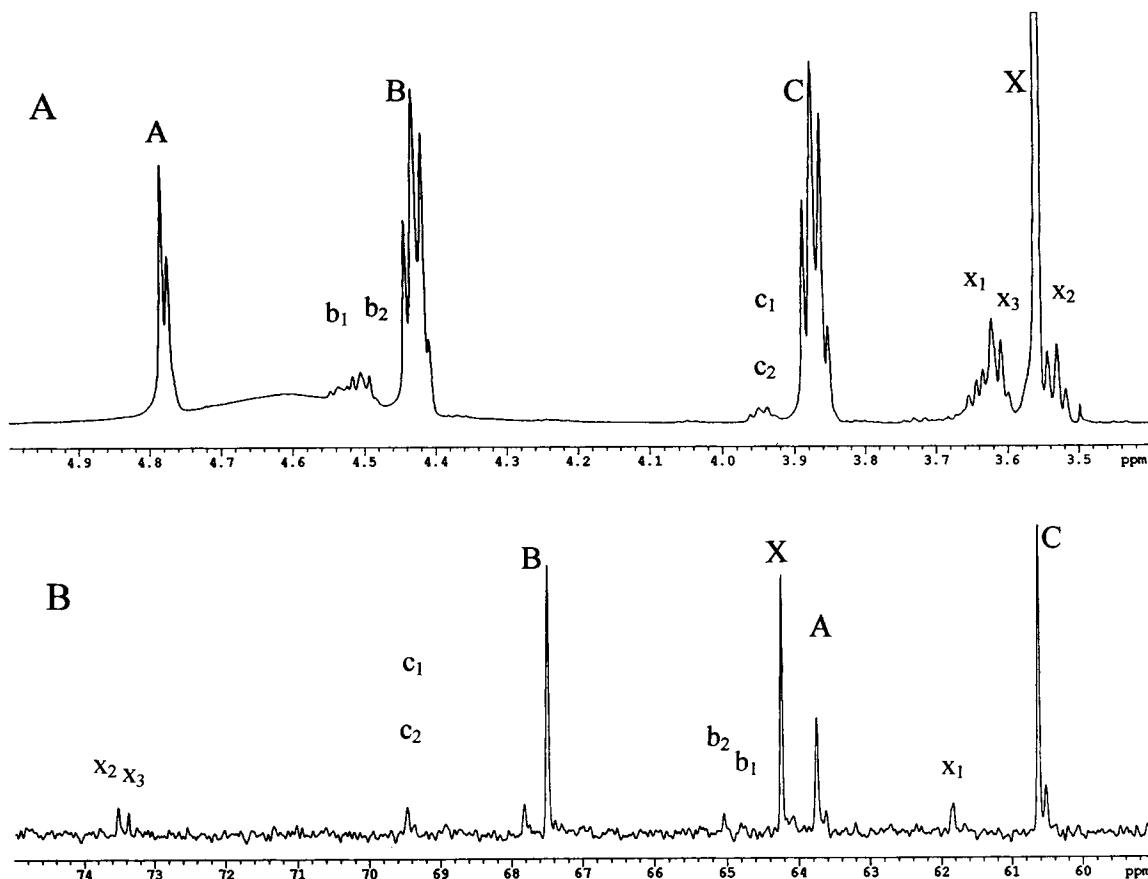
### Synthesis

To synthesize HEB, initial reactions were carried out by refluxing BDA with a large excess of ethylene glycol. BDA is not soluble even in boiling ethylene glycol and the esterification did not take place under reflux conditions. Reactions of BDA and ethylene glycol were then conducted under more severe conditions either by increasing the reaction temperature and pressure or by the use of esterification catalysts.<sup>22</sup>

Esterification of BDA, without any catalyst, did take place when the temperature and pressure were increased to about 240°C and 480 kPa, respectively. Reactions were carried out utilizing ratios of BDA/ethylene glycol ranging from 1 : 2 to about 1 : 4 and the products were analyzed for diethylene glycol by GC. As expected, under the

same reaction conditions, the amount of diethylene glycol in the product increased with the increasing amount of ethylene glycol in the reaction but the slurry of BDA in ethylene glycol was relatively difficult to handle at low ethylene glycol levels. The most suitable ratio of BDA/ethylene glycol from the point of view of handling and low diethylene glycol content was 1 : 2.2.

Esterification of BDA with ethylene glycol was also investigated using small amounts of titanium isopropoxide, Tyzor® (i-propoxy[triethanolaminate]Ti), dibutyltin oxides, butyltin chloride dihydroxide [BTCl(OH)<sub>2</sub>], and triiodophenol as the catalyst. Screening of the catalysts was done by refluxing BDA and the catalyst in a large excess of ethylene glycol. Since BDA is insoluble in ethylene glycol, and HEB is soluble under the same conditions, the progress of the reaction is easily monitored by the clarity of the reaction mass; initial slurry of BDA in ethylene glycol clears as the reaction proceeds. Depending on the catalyst, the reaction was completed in 1–4 h. Titanium isopropoxide gave the best results, as the reaction was complete in 1 h. HEB and the oligomer, which crystallized on cooling, were analyzed for diethylene glycol after filtration and drying. Figure 1 gives the reaction time and the amount of diethylene glycol produced using different catalyst systems. Although we have found no quantitative relationship between the reaction time and



**Figure 3** (A) 400 MHz  $^1\text{H}$ -NMR spectrum and (B) 100 MHz  $^{13}\text{C}$ -NMR spectrum of typical oligomer prepared from BDA, terephthalic acid, and ethylene glycol without catalyst. The labeled peaks are identified in Table II.

the diethylene glycol content, it appeared that highly acidic catalysts like triiodophenol catalyzed the formation of diethylene glycol as well as the esterification reaction. Since the reaction time and the formation of diethylene glycol was lowest with titanium isopropoxide, further experiments were carried out to find the optimum reaction conditions. Different amounts of titanium isopropoxide were used at the ethylene glycol reflux temperature and the reaction time for HEB formation was measured. Figure 2 shows that the reaction time decreases linearly as the catalyst level increases from 60 to 600 ppm, but that further increase of the catalyst concentration does not have any significant effect on the reaction time.

### Composition by NMR Spectroscopy

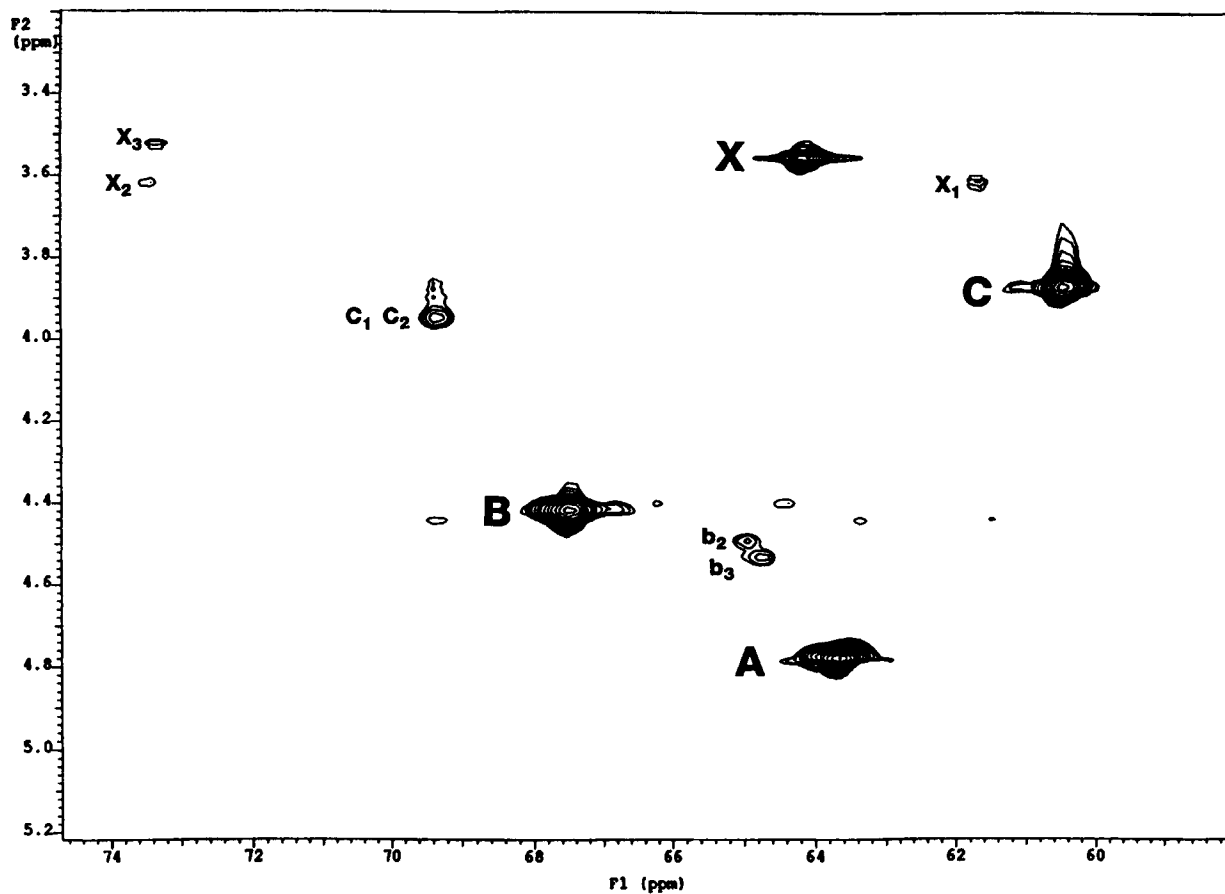
#### *HEB Synthesized with Catalyst*

The  $^{13}\text{C}$  spectrum of the sample prepared with the catalyst was predominantly due to HEB. Prominent

peaks at 166.2, 144.1, 130.4, 130.3, 127.5, 67.5, and 60.6 ppm were assigned to carboxylate carbon, to aromatic  $\text{C}_4$ ,  $\text{C}_{2,6}$ ,  $\text{C}_1$ , and  $\text{C}_{3,5}$  carbons, to ester methylene ( $^1\text{H}$ : 3.94 ppm), and to terminal methylene ( $^1\text{H}$ : 4.47 ppm) carbon, respectively. Weaker peaks at 63.7 ppm ( $^1\text{H}$ : 4.76 ppm) and 64.2 ppm ( $^1\text{H}$ : 3.64 ppm) were attributed to a small amount (7% m/m) of ethylene glycol dicarboxylate (species A in Table II) and to unreacted ethylene glycol, respectively.

#### *HEB Synthesized Without Catalyst*

The  $^1\text{H}$ -NMR spectrum [Fig. 3(A)] of the methylene protons of ethylene glycol-terephthalic acid and ethylene glycol-BDA oligomer consisted of several major peaks (identified with capital letters in Table II) which were flanked by peaks of much lower intensity. The major peaks were assigned by their chemical shifts<sup>11</sup> to free ethylene glycol (X), ethylene glycol reacted at our hydroxyl group (B, methylene  $\alpha$  to ester bond; C, methylene  $\beta$  to ester bond), and

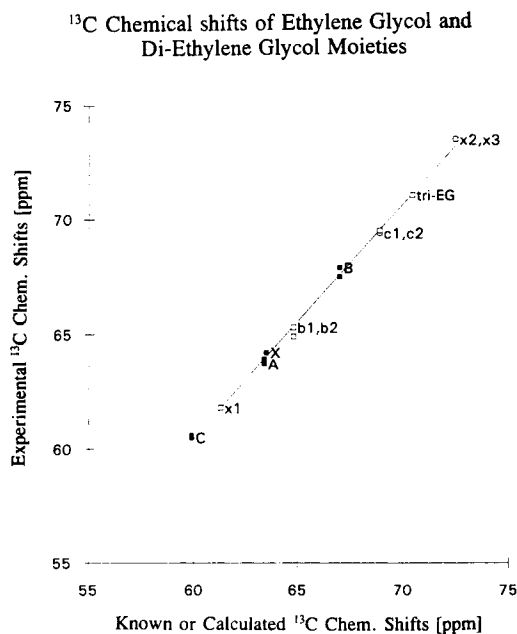


**Figure 4** One-bond heteronuclear correlation spectrum (HMOC) of typical oligomer prepared from BDA, terephthalic acid, and ethylene glycol without catalyst. The labeled peaks are identified in Table II.

**Table III** Chemical Shift Calculations

Type of Methylene Group	Calcd (ppm)	Exp (ppm)
HO—CH <sub>2</sub> —CH <sub>2</sub> —OH	63.5 <sup>a</sup>	64.2
—COO—CH <sub>2</sub> —CH <sub>2</sub> —OH	67.0	67.5–67.9
—COO—CH <sub>2</sub> —CH <sub>2</sub> —OH	59.9	60.5–60.6
—COO—CH <sub>2</sub> —CH <sub>2</sub> —OOC	63.4	63.7–67.9
HO—CH <sub>2</sub> —CH <sub>2</sub> —O—CH <sub>2</sub> —CH <sub>2</sub> —OH, COO—CH <sub>2</sub> —CH <sub>2</sub> —O—CH <sub>2</sub> —CH <sub>2</sub> —OH	61.3 <sup>a</sup>	61.8
HO—CH <sub>2</sub> —CH <sub>2</sub> —O—CH <sub>2</sub> —CH <sub>2</sub> —OH, COO—CH <sub>2</sub> —CH <sub>2</sub> —O—CH <sub>2</sub> —CH <sub>2</sub> —OH	72.5 <sup>a</sup>	73.4–73.5
—COO—CH <sub>2</sub> —CH <sub>2</sub> —O—CH <sub>2</sub> —CH <sub>2</sub> —OH, —COO—CH <sub>2</sub> —CH <sub>2</sub> —O—CH <sub>2</sub> —CH <sub>2</sub> —COO—	64.8	64.8–65.4
—COO—CH <sub>2</sub> —CH <sub>2</sub> —O—CH <sub>2</sub> —CH <sub>2</sub> —OH, —COO—CH <sub>2</sub> —CH <sub>2</sub> —O—CH <sub>2</sub> —CH <sub>2</sub> —OOC—	68.9	69.4–69.5
—O—(CH <sub>2</sub> ) <sub>2</sub> —O—CH <sub>2</sub> —CH <sub>2</sub> —O—(CH <sub>2</sub> ) <sub>2</sub> —	70.5 <sup>a</sup>	71.1

<sup>a</sup> Average literature value.



**Figure 5** Experimental vs. calculated and/or published  $^{13}\text{C}$  chemical shifts. The labeled peaks are identified in Tables II and III.

ethylene glycol reacted at both ends (A). The low intensity peaks (lower-case letters in Table II) were assigned through the  $^{13}\text{C}$  spectrum [Fig. 3(B)], as described below. The hydroxyl protons were responsible for the broad absorption at 4.6 ppm.

The chemical shifts of corresponding methylene  $^{13}\text{C}$  atoms of ethylene glycol-terephthalic acid and ethylene glycol-BDA oligomer differed by less than 0.4 ppm from each other. The identification of the major peaks followed from the  $^1\text{H}$  peak assignments by inspection of the  $^1\text{H}$ - $^{13}\text{C}$  HMQC correlation map (Fig. 4). Starting from these chemical shifts, we calculated that replacement of the hydroxyl group of ethylene glycol with the ester linkage to terephthalic acid or BDA shifted the peak of the  $\alpha$ -methylene carbon by an average of +3.5 ppm and of the  $\beta$ -carbon by -3.6 ppm. Double substitution resulted in a -0.4 ppm shift as determined experimentally. With this information, we calculated the chemical shifts of the methylene carbons of ethylene glycol dimers at different degrees of esterification. The results are listed in Table III together with the average literature values of chemical shifts of mono-, di-, and triethylene glycol and with the experimental chemical shift data of this work. Calculated vs. experimental peak positions are plotted in Figure 5. The experimental chemical shifts agreed well with calculated shifts and with average shifts from the literature (correlation coefficient: 0.9967; standard

error of the calculated chemical shift:  $\pm 0.2$  ppm). Furthermore,  $T_1$  inversion recovery data confirmed the overall peak assignment;  $T_1$  increased with the distance separating the methylene carbon from the ester linkage. The interpretation of the weak peaks in terms of free diethylene glycol and of diethylene glycol with one and of diethylene glycol with two ester linkages was therefore well founded. The  $^1\text{H}$  chemical shifts of the weak peaks followed from the established  $^{13}\text{C}$  peak assignments by using the HMQC correlation map (Table II).

The peak areas of the assigned  $^{13}\text{C}$  peaks were used to calculate the distribution of ethylene glycol and diethylene glycol moieties in the oligomer. The integration of  $^{13}\text{C}$  spectra of concentrated polymer solutions, though quite commonly carried out, is beset with pitfalls.<sup>16-19</sup> Of particular concern in this instance was the wide dynamic range of peak intensities resulting in large differences of signal-to-noise ratio between the peaks of ethylene glycol and diethylene glycol. This explains the large errors attached to the composition values given in Table IV. The mol % of diethylene glycol (mol diethylene glycol divided by mol of diethylene glycol + ethylene glycol) was remarkably constant over a wide range of noncatalytic preparation conditions, with only two exceptions: First, addition of triethylamine resulted in the lowest diethylene glycol level (2.8%); second, excess ethylene glycol in the feed resulted in an exceptionally high diethylene glycol level (10.6%). Note that in the sample prepared by the catalytic process the formed diethylene glycol was

**Table IV** Distribution of Ethylene Glycol in Various Oligomers

	Diethylene Glycol <sup>a</sup> (Mol %)	Endgroups <sup>b</sup> (Mol %)
Thermal process, terephthalic acid		
normal ethylene glycol	7.6 $\pm$ 0.7	74 $\pm$ 3
excess ethylene glycol	10.6 $\pm$ 1.6	81 $\pm$ 6
Thermal process, BDA		
+2% terephthalic acid	8.6 $\pm$ 1.1	79 $\pm$ 6
+10% terephthalic acid	7.5 $\pm$ 0.3	81 $\pm$ 3
+2% terephthalic acid + TEA	2.8 $\pm$ 0.4	79 $\pm$ 5
+10% terephthalic acid + exc. ethylene glycol	6.1 $\pm$ 0.9	81 $\pm$ 5
Catalytic process, HEB	0	100

<sup>a</sup> 100 · diethylene glycol / (ethylene glycol + diethylene glycol).

<sup>b</sup> 100 · (diethylene glycol + ethylene glycol)<sub>endgroup</sub> / ethylene glycol.

below the detection level of the experiment. The third column of Table IV shows the percentage of ethylene glycol and diethylene glycol units which are endgroups. The deviations from 100% show that a considerable number of ethylene glycol and diethylene glycol groups are functionalized at both alcohol ends.

## CONCLUSIONS

GC and NMR analysis showed that the formation of diethylene glycol was almost completely suppressed when the reaction of BDA with ethylene glycol was carried out in the presence of a catalyst instead of under high pressure and at high temperature. Under noncatalytic conditions, the percentage of diethylene glycol moieties ranged from 3 to 11%, and a sizable number of glycol units (ethylene glycol and diethylene glycol) were functionalized at both alcohol groups. The experimental conditions did not greatly influence the composition of the oligomer, except when a large excess of ethylene glycol was used (which caused more diethylene glycol formation), and when triethylamine was added to prevent diethylene glycol formation.

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