

## Organosoluble Oligomer Obtained by Glycolysis of Poly(ethylene terephthalate) and Its Detailed Structural Characterization by MALDI-TOF Mass Spectrometry

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**ABSTRACT:** Organosoluble oligomers were obtained by the depolymerization of poly(ethylene terephthalate) with an aliphatic glycol at 260–280°C and then characterized by <sup>1</sup>H NMR, gel permeation chromatography (GPC), and matrix assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS). The detailed analysis of their spectrum revealed that for an aliphatic primary diol, the transesterification smoothly occurred in the reaction media.

**KEY WORDS** Poly(ethylene terephthalate) / Glycolysis / Organosoluble Oligomer / MALDI-TOF Mass Spectrometry /

Poly(ethylene terephthalate), PET, is widely used for synthetic fibers and film and recently its use in the production of soft drink bottles has been dramatically increasing. The efficient utilization of waste PET resulting from its huge production is a very important issue and there has been a growing tendency to effectively recycle it. PET possessing an ester linkage is a suitable material for feedstock recycling and many methods using chemical degradation have already been reported,<sup>1,2</sup> along with that of mechanical recycling. The recycling methods are mainly divided into alcoholysis (methanolysis and glycolysis) and hydrolysis, and the methanolysis process which produces dimethyl terephthalate (DMT) and ethylene glycol (EG) has already been adopted in some companies. The glycolysis process has been also well studied using EG to obtain *bis*-hydroxyethyl terephthalate (BHET) which can be used as a substrate for PET synthesis. Partial PET glycolysis depending on the ratio between the PET and glycol, reaction time, and reaction temperature is also an important process and the process using EG as a glycol usually produces BHET and oligomers having molecular weights less than 1000, both of which are quite useful materials for the synthesis of unsaturated polyesters and polyurethanes.<sup>3</sup> Recently, as a new entry for the useful utilization of the glycolysis products, we have demonstrated the synthesis of a copolyester by polycondensation between the glycolysis products and copoly(succinic anhydride-ethylene oxide).<sup>4</sup> We have also reported as a patent that various vinyl-terminated macromonomers, which would be useful for paintings, adhesives, and so on, were synthesized from the glycolysis products.<sup>5</sup> For the design and synthesis of the

useful macromonomers, it is essential to grasp the detailed character of glycolysis products. Furthermore, to our knowledge, little attention has ever been paid to the glycolysis products with higher molecular weights, which usually have a low solubility in organic solvents and a high viscosity. In this report, as a research for characterizing the various glycolysis products in detail, we would like to describe the novel soluble higher oligomers obtained by the glycolysis using aliphatic diols and their structural characterization by MALDI-TOF mass spectrometry.

### EXPERIMENTAL

#### *Materials and Reagents*

PET pellets (*ca.* 4 mm (length) *ca.* 2 mm (diameter), Kanebo Gohsen, Ltd., EFG6C, 0.7 dL g<sup>-1</sup>) were used for the degradation reaction. Glycols, tetraethylene glycol, 1,4-butanediol, 1,6-hexanediol, dipropylene glycol, and solvents, *i.e.*, MeOH, CHCl<sub>3</sub>, tetrahydrofuran (THF), dimethylformamide (DMF), acetone, and hexafluoroisopropanol (HFIP) were used without further purification.

#### *General Procedure of Glycolysis and Characterization of Obtained Oligomers*

PET pellets (30 g: 0.16 mol (PET monomer unit)) and a glycol (0.15 mol) were put into a 1 L flask and the flask was heated to *ca.* 260–280°C by a mantle heater until the pellets were completely melted. After stirring at 260–280°C for 0.5–2 h, the reaction mixture was cooled, partly dissolved into CHCl<sub>3</sub> (30 mL), and then poured into MeOH (*ca.* 800 mL). The precipitations were filtered, washed with MeOH, and dried

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**Table I.** Results of PET glycolysis

Entry	Sample Name	Glycol	Oligomers insoluble in MeOH (OIM)						Oligomers soluble in MeOH (OSM)					
			Time/hr <sup>a</sup>	Yield/% <sup>b</sup>	AV <sup>c</sup>	OHV <sup>d</sup>	$M_n^e$	$M_w/M_n$ [TP]/[Gly] <sup>f</sup>	Yield/% <sup>g</sup>	AV <sup>c</sup>	OHV <sup>d</sup>	$M_n^e$	$M_w/M_n$	
1	TEEG05	Tetraethylene glycol	0.5	23	0.07	1.0	1871	1.33	–	52	0.13	3.5	873	1.35
2	14BU05	1,4-Butanediol	0.5	58	0.14	1.1	–	–	84/16	19	0.39	5.1	562	1.13
3	14BU10	1,4-Butanediol	1.0	54	0.17	1.3	–	–	74/26	29	0.40	5.4	565	1.14
4	16HEX05	1,6-Hexanediol	0.5	47	0.08	1.5	–	–	81/19	39	0.09	7.8	656	1.15
5	16HEX10	1,6-Hexanediol	1.0	38	0.04	1.2	1623	1.20	66/34	56	0.07	6.4	567	1.34
6	16HEX20	1,6-Hexanediol	2.0	43	0.03	1.3	2073	1.23	57/43	40	0.06	3.7	725	1.20
7	DPG10	Dipropylene glycol	1.0	59	–	–	–	–	97/3	2	0.21	2.2	743	1.16
8	DPG20	Dipropylene glycol	2.0	55	–	–	–	–	90/10	7	0.13	5.2	709	1.14

<sup>a</sup>Reaction time, <sup>b</sup>Weight of OIM/weight of PET pellets and glycol  $\times 100$ , <sup>c</sup>Acid value/mol  $\text{kg}^{-1}$ , <sup>d</sup>Hydroxyl value/mol  $\text{kg}^{-1}$ , <sup>e</sup>Determined by GPC, based on polystyrene standard, <sup>f</sup>[TP]/[Gly] = Molar ratio of [terephthalate]/[glycol] determined by <sup>1</sup>H NMR spectra, <sup>g</sup>Weight of OSM/weight of PET pellets and glycol  $\times 100$ .

at 60°C under reduced pressure for 24 h. The filtrates were combined, evaporated under reduced pressure, and dried at 60°C under reduced pressure for 24 h. Both the precipitation part and the filtration part were characterized by <sup>1</sup>H NMR, gel permeation chromatography (GPC), and matrix assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS). The hydroxy value and the acid value were also measured by the method described below. The <sup>1</sup>H NMR measurements were carried out using a Varian UNITY plus-400 (400 MHz) spectrometer and the chemical shifts were represented as  $\delta$  values to the internal standard tetramethylsilane. Molecular weights relative to poly(styrene) standards were determined by GPC (Waters 150CV system equipped with a Ultrastaygel<sup>®</sup>, Linear, 10<sup>4</sup> Å and 500 Å column) using THF as the mobile phase at 40°C. The flow rate was 1 mL min<sup>-1</sup>. The MALDI-TOF-MS measurement was performed on a KRATOS COMPACT MALDI IV in the linear mode. The spectrometer equipped with a nitrogen laser (337 nm, 3 ns) was calibrated using Cytochrome C (horse heart), Bovine Insulin, Angiotensin II, and sodium. 2,5-Dihydroxybenzoic acid was used as the matrix and in each MALDI experiment, the samples were prepared by depositing an oligomer solution (*ca.* 1 mg mL<sup>-1</sup> THF or *ca.* 30 mg mL<sup>-1</sup> HFIP) and a THF solution of the matrix on a sample plate.

The acid values (AV) were calculated based on the titration of a solution (50 mL) of oligomers (*ca.* 50–100 mg) dissolved in a THF or THF:CHCl<sub>3</sub> (1 : 1) with 0.01N KOH-ethanol solution using bromothymol blue as the indicator. The hydroxy values (HV) were determined as follows. Thus, the oligomers (*ca.* 1.0 g) and phthalic anhydride (0.01 mol) were dissolved in pyridine (20 mL) and these mixtures were stirred at 60–70°C for 1 h. Water (10 mL) was added and the mixtures were stirred for 3 min. The obtained reaction mixtures were titrated with a 1N NaOH-aqueous solution using a phenolphthalein as the indicator. The hydroxy

values were calculated using the following equation.

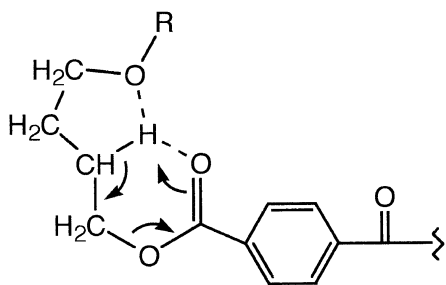
$$\text{HV (mol kg}^{-1}\text{)} = (\text{B}-\text{C})/\text{A}$$

A: sample weight (g), B: titration value (mL) in the blank experiment carried out without using any oligomers. C: titration value (mL) in the experiment carried out using an oligomer.

## RESULTS AND DISCUSSION

PET has a poor solubility in organic solvents due to the stiffness of its molecule, *i.e.*, the low aliphaticity and the lack of flexibility of ethylene glycol. Therefore, the use of a glycol possessing a long carbon chain would lead us to solve such a solubility problem and also has an advantage for reprecipitation using methanol, which enables us to obtain oligomers with a narrow dispersity. Thus, glycolysis of PET was carried out using tetraethylene glycol, 1,4-butanediol, 1,6-hexanediol, and dipropylene glycol, and the reaction mixtures were separated into the soluble and insoluble parts in methanol by the reprecipitation method. The obtained results are summarized in Table I. The oligomers insoluble in methanol (OIM) were obtained as a solid in moderate to good yields, while the oligomers soluble in MeOH (OSM) were produced as a pasty compound. The sum of the yields of OIM and the OSM was over 75%, except for DPG10 and DPG20.<sup>6</sup>

The acid values (AV) of OSM were in all cases higher than those of OIM, and the oligomers obtained by degradation with 1,6-hexanediol showed the lowest acid values in both OIM and OSM, while those by 1,4-butanediol showed highest values of all the oligomers. A carboxylic acid function would mainly be produced by  $\beta$ -elimination of an ester moiety<sup>7</sup> and this reaction would contribute to the high AV of OSM. Furthermore, for 1,4-butanediol,  $\beta$ -elimination would be significantly accelerated by the participation of a hydroxyl group in the transition state, as shown in Figure 1.



**Figure 1.** Plausible mechanism of  $\beta$ -elimination for 1,4-butanediol.

**Table II.** Solubility of OIM in various solvents<sup>a</sup>

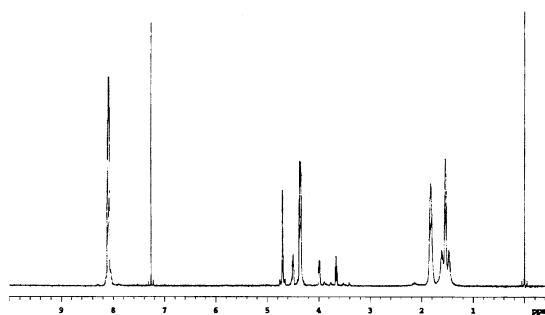
Oligomers	THF	CHCl <sub>3</sub>	DMF	Acetone
TEEG05	○	○	○	×
14BU05	×	×	×	×
14BU10	×	×	×	×
16HEX05	×	×	×	×
16HEX10	○	○	○	×
16HEX20	○	○	○	×
DPG10	×	×	×	×
DPG20	×	×	×	×

<sup>a</sup>The experiments were carried out using 10 mg of each oligomer in 10 mL of each solvent. ○: completely soluble, ×: insoluble.

The OH values of all the OIMs were much lower than the results reported by Orbey and other researchers, in which BHET and lower oligomers were main glycolysis products<sup>8</sup> and based on these results, it is obvious that the glycolysis at 260–280°C, using one equivalent of a glycol, followed by the reprecipitation by MeOH, gives higher oligomers in good yield. A detailed discussion about the molecular weight of OIM will be described below.

The solubility tests of OIM were carried out with THF, CHCl<sub>3</sub>, DMF, and acetone, and the results are summarized in Table II. TEEG05, 16HEX10, and 16HEX20 showed good solubility in THF, CHCl<sub>3</sub>, and DMF, while the other oligomers did not dissolve in any of the organic solvents. Based on these results, it is clear that tetraethylene glycol and 1,6-hexanediol are suitable glycols in order to obtain soluble oligomers derived from PET. In fact, the glycolysis of 1,6-hexanediol is recommended, due to the low yield of TEEG05.

The GPC measurement was able to be carried out in all the OSM samples, however for OIM, the low solubility of 14BU05, 14BU10, 16HEX05, DPG10, and DPG20 in THF prevented us from estimating their molecular weight by GPC. The number average molecular weight of OIM were *ca.* 2000 and those of OSM were less than 900 and it was found that in order to show sufficient insolubility in MeOH, an oligomer should have a number average of molecular weight



**Figure 2.** <sup>1</sup>H NMR spectrum of 16HEX20 (OIM).

above *ca.* 1000 (Table I). When comparing the OIM results, the Mn of 16HEX20 was slightly greater than that of 16HEX10 and these results easily led us to the idea that transesterification would preferably occur rather than glycolysis after 1 h. The idea is well supported by the analysis of their <sup>1</sup>H NMR and MALDI-TOF-MS spectra described below.

#### <sup>1</sup>H NMR Analysis of OIM

The <sup>1</sup>H NMR spectrum of the OIM obtained by the glycolysis with 1,6-hexanediol for 2 h is shown in Figure 2. In addition to the signal of both terephthalic acid ( $\delta$  8.1 ppm) and ethylene glycol ( $\delta$  4.7 ppm), the signal of the carbon chain of 1,6-hexanediol was clearly found around  $\delta$  1–2 ppm and other signals assignable to the methylene part next to the oxygen function also clearly appeared around  $\delta$  3–4.6 ppm.

The mixtures of hexafluoroisopropanol (0.1 mL) and CDCl<sub>3</sub> (1.0 mL) were employed as a solvent for the measurement of the <sup>1</sup>H NMR of 14BU05, 14BU10, 16HEX05, DPG10, and DPG20, all of which showed low solubility in other common organic solvents. The analysis of the integral values of both the terephthalic acid part and that of the glycol added part are also summarized in Table I. The glycol content in oligomers apparently increased, especially in a primary diol such as 1,4-butanediol and 1,6-hexanediol, with the reaction time being longer. These results clearly indicated that the transesterification efficiently occurred in the reaction media. The above NMR analysis also disclosed that an oligomer should have over a 30% content of 1,6-hexanediol in its structure in order to have enough solubility toward THF, CHCl<sub>3</sub>, and DMF. On the other hand, the dipropylene glycol content in the obtained oligomers was extremely low and these results suggested that the oligomers have a dipropylene glycol unit only in their terminal and not internally. Propylene glycol and dipropylene glycol, which have a branched alkyl group in their structure, are usually used in order to reduce the crystallization of the polyesters and to increase the solubility in organic solvents by decreas-

ing the regularity of the carbon chain. In this case, the secondary hydroxyl group would prevent further transesterification and it would be difficult to obtain soluble oligomers having a relatively high molecular weight by the glycolysis of such a glycol.

#### MALDI-TOF-MS Analysis

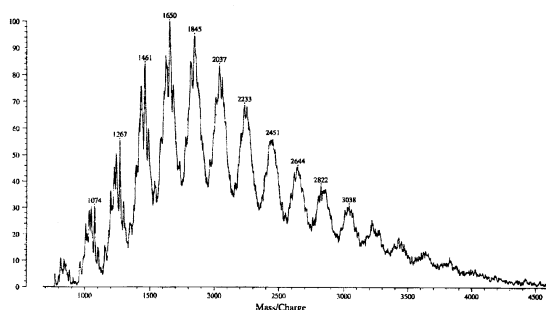
Although, by a GPC method, the data concerning the molecular weight could not be obtained for the OIM of 14BU05, 14BU10, 16HEX05, DPG10, DPG20, the MALDI measurement was possible for all the OIMs, using hexafluoroisopropanol as the dissolving solvent. As a representative result, the spectra of OIM 14BU05 is shown in Figure 3. The molecular weights of the oligomers were distributed from 1000 to 4000 Da and each group of peaks differed by *ca.* 200 Da which is in good agreement with the molecular weight of the PET monomer 192. Similar distributions of the molecular weight were observed in the spectrum of 14BU10, 16HEX05, 16HEX10, 16HEX20, DPG10, and DPG20.

We also investigated the detailed structure of the obtained oligomers by MALDI TOF-MS with reducing the power of a nitrogen laser in order to prevent fragmentation of the molecular ions. The measurement was performed using a concentrated solution (*ca.* 30 mg mL<sup>-1</sup>). The results with OIM obtained by glycolysis with 1,6-hexanediol are summarized in Figure 4. All the major peaks were the sodium cationized oligomers. In Figure 4, the six different series of peaks (A–F), each of which differed by 192 Da that correspond to the repeating unit of PET, are identified and each series can be written as

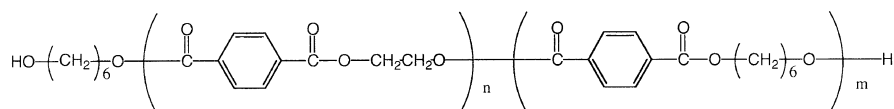
$$M = 192n + 248m + 118 + 23$$

$$(A : m = 0; B : m = 1; C : m = 2; D : m = 3;$$

$$E : m = 4; F : m = 5)$$



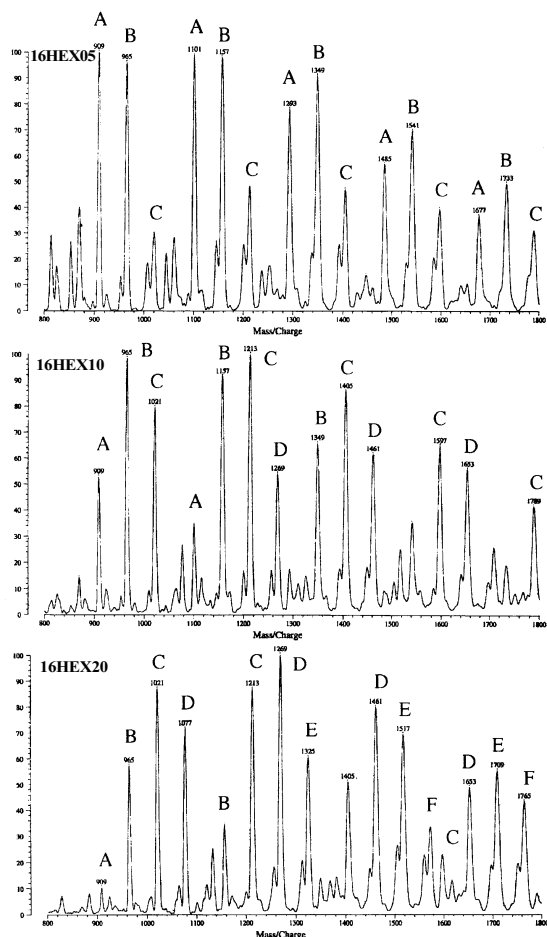
**Figure 3.** MALDI-TOF mass spectra of 14BU05 (OIM).



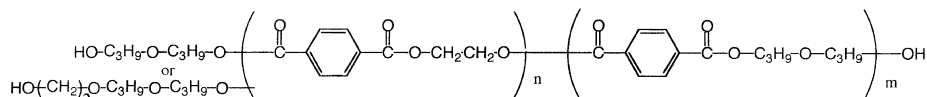
**Figure 5.** Chemical structure of the oligomer obtained by glycolysis with 1,6-hexanediol.

where 248, 118, and 23 Da are the masses of the 1,6-hexylene terephthalate units, 1,6-hexanediol, and sodium and *n* and *m* are the numbers of the 1,6-hexylene terephthalate units and the ethylene terephthalate units, respectively (Figure 5). For example, 909, 965, and 1021 Da are assigned as **A** (*n* = 4), **B** (*n* = 3), and **C** (*n* = 2). In the spectra of 16HEX30, the series **A** and **B**, in which the proportion of EG is much higher than that of 1,6-hexanediol is the main one, and the series gradually shifts from **A** and **B** to the other ones (**C**–**F**) which contain more 1,6-hexanediol units in their structure as the reaction time becomes longer (30 min – 1 h – 2 h). These results clearly point out that the depolymerization of PET has almost finished in 30 min and then the exchange of a glycol between the ethylene glycol and 1,6-hexanediol effectively proceeds.

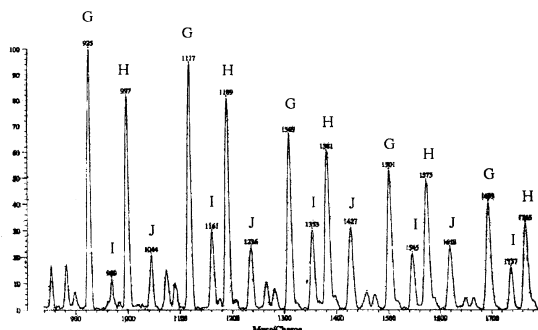
The MALDI spectra of DPG20 are shown in Figure 6. The four series of peaks (**G**–**J**) can be identi-



**Figure 4.** MALDI-TOF mass spectrum of OIM oligomers, 16HEX05, 16HEX10, and 16HEX20.



**Figure 7.** Chemical structure of the oligomer obtained by glycolysis with dipropylene glycol.



**Figure 6.** MALDI TOF mass spectrum of DPG20 (OIM).

fied and each series differed by 192 Da, the same as the spectra of 16HEX05, 16HEX10, and 16HEX20 described above. Each series can be expressed by

$$M = 192n + 264m + 134 + 23 \text{ (G : } m = 0; \text{H : } m = 1)$$

$$M = 192n + 264m + 178 + 23 \text{ (I : } m = 0; \text{J : } m = 1)$$

where 264, 134, and 178 Da are the mass of the dipropylene terephthalate units, dipropylene glycol, and the compound formed during the condensation between dipropylene glycol and EG by the loss of  $\text{H}_2\text{O}$ , respectively and  $m$  is the number of the dipropylene terephthalate units (Figure 7). For example, 925 and 969 Da are assigned as **G** ( $n = 4$ ) and **I** ( $n = 4$ ). In all the series, the proportion of EG in the molecule was much higher than that of dipropylene glycol. Therefore, a dipropylene glycol unit would be introduced in only their terminal and the transesterification did not proceed at all even after a 2 h treatment with dipropylene glycol. These results are in good agreement with the results of  $^1\text{H}$  NMR spectrum. Thus, the low solubility of the oligomers depolymerized by DPG is due to the low DPG content in the oligomers, which results from the lack of transesterification ability.

## CONCLUSION

In summary, we obtained soluble oligomers having

a number average molecular weight over 2000 by the glycolysis of PET with 1,6-hexanediol. The analysis of the results from the  $^1\text{H}$  NMR and MALDI-TOF-MS spectra revealed that the transesterification is an important factor to obtain the soluble oligomers and the 1,6-hexanediol content in the oligomers is needed to be over 30% for sufficient solubility. The oligomers obtained here have a promising potential as a telechelic oligoester and their application is now under investigation.

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