Characterization of Novel Biodegradable Copolyesters Prepared from Glycolyzed Products of Poly(ethylene terephthalate)

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ABSTRACT: Poly(ethylene terephthalate), PET reacted with various glycols in the presence of titanium tetraisopropoxide as a catalyst. The glycolyzed PET was fractionated into two parts—soluble and insoluble in $CHCl_3$—characterized and used as a raw material to synthesize copolyesters. The soluble part in the $CHCl_3$ part was a mixture of monomers and oligomers, and no melting points were observed. On the other hand, in the insoluble part a melting point was determined. The glycolyzed PET and copoly(succinic anhydride/ethylene oxide), PES were condensed to produce copolymers. The synthesized copolyesters were amorphous and hydrolyzed enzymatically due to a decrease in the crystallinity. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 1838–1847, 2002; DOI 10.1002/app.10462

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INTRODUCTION

The continuously increasing extent of pollution of the environment has recently given rise to demands either for novel biodegradable polymer[1–7] or for recycling.[8]

The growing interest in poly(ethylene terephthalate)(PET) recycling is due to the widespread use of packing made of this polymer—mainly as bottles. The polymer recycling is one of the most important topics both for environmental protection and reduction of consumption of energy resources. However, the development of an economically viable polymer recycling processes is essential for establishing a society geared to recycling in the nearest future.

The recycling of waste polymers including PET can be carried out in various ways. A very attractive recycling method of used polymer materials is the so-called "materials recycling," which consists of many processes such as collection, washing, sorting, drying, melting, and repelletizing. The recyclate cannot practically compete, properties wise, with the respective virgin materials.

Among other methods of polymer recycling, chemical recycling is of major importance. The availability of a large variety of products, for example, monomers for polymers and other additive for polymers, stand for some of the advantages of PET chemical recycling. PET waste was easily decomposed by glycolysis with glycols having low molecular weight such as ethylene glycol (EG),

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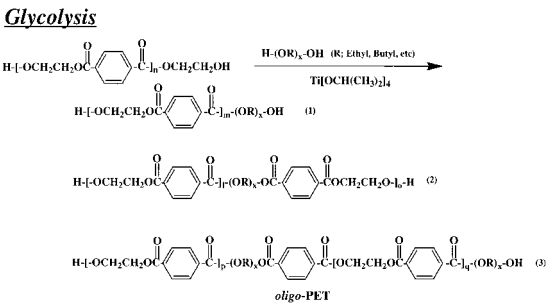
propylene glycol (PG), and diethylene glycol (DEG). Therefore, in recent years the use of PET waste for low-tonnage production of specialized products such as raw materials for syntheses of saturated and unsaturated polyesters, polyurethanes, and additives has become of major interest.[9–14]

On the other hand, biodegradable polyesters such as poly(L-lactide),[15,16] poly(butylene succinate),[17] and poly(ε-caprolactone)[18] are now widespread. Moreover, biodegradable polymers containing terephthalyl moiety are commercially available.[19]

In the present investigation, PET was depolymerized with glycols such as tetraethylene glycol (TEEG), poly(ethylene glycol) (M_n = 400) (PEG400), poly(tetramethylene oxide) (M_n = 650) (PTMO650), or terpoly[poly(oxyethylene)-poly(oxypropylene)-poly(oxyethylene)] (M_n = 1100) (Pluronic L31) having higher molecular weight than the foregoing three glycols to obtain the oligomeric glycolyzed PET. The copolyesters were prepared by a polycondensation of glycolyzed PET with copoly(succinic anhydride/ethylene oxide) (PES) and characterized by GPC, ^{1}H-NMR, and DSC. Biodegradabilities of the resultant copolyesters were evaluated with hydrolysis such as enzymes (lipases) or activated sludge.



Scheme 1

EXPERIMENTAL

Materials

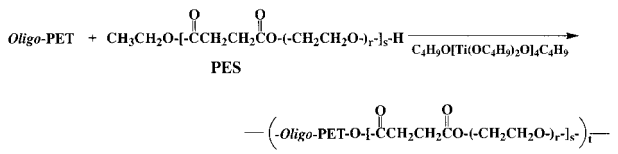
The chips of PET homo polymer were obtained from Kanebo Gosen Co. (BELLPET-EFG6C) with an intrinsic viscosity [η], of 0.7 (dL/g) in trifluoroacetic acid (CF_3COOH) at 30°C. TEEG, PEG400, and PTMO650 (from Wako Pure Chemical Co., Japan) were used as received. Pluronic L31 was obtained from Asahi Denka Co. Titanium tetraisopropoxide (TIP) and Titanium tetrabutoxide, tetramer (TTBT) were obtained from Wako Co. PES (M_n = 6500) were prepared by a ring-opening copolymerization using $Mg(OEt)_2$ as described in our previous article.[20–22] The enzyme employed for biodegradation tests was a lipase from *Rhizopus arrhizus* (Boehringer-Mannheim). Standard activated sludge was offered from Chemical Inspection & Testing Institute, Japan. Other chemicals were obtained from Wako Pure Chemical Co. Japan.

PET Glycolysis (Scheme 1)

A representative example of a glycolysis of PET is the following one: glycolysis was carried out with a three-necked round-bottom flask of 1-L capacity having a reflux condenser, thermometer, and stirrer assembly. The procedure was loading 20 g of PET, 15 g of TEEG, and catalyst (0.5% w/w TIP based on PET), followed by reacting at about 220°C under reflux for 8 h. The reactor and contents were cooled down to ambient temperature. A large quantity of $CHCl_3$ was added to dissolve the reaction products. The $CHCl_3$ solution was filtered. The filtrate containing products and free TEEG was concentrated by evaporation of $CHCl_3$, followed by immersion in CH_3OH to remove free TEEG. The CH_3OH solution was filtered with glass filter (G-2), and the glycolyzed products were dried under reduced pressure at 70°C for 24 h. The insoluble part in the $CHCl_3$ was dissolved in CF_3COOH. The CF_3COOH solution was poured dropwise in acetone and precipitated. The acetone solution was filtered with glass filter (G-2). The insoluble part in $CHCl_3$ was dried under vacuum at 70°C for 24 h. The glycolyzed products were then analyzed for hydroxyl value and acid value as follows: (a) the hydroxyl values were determined by conventional acetic anhydride/pyridine mixture, and (b) the acid values were determined by titrating solution of the sample in toluene, with standard alcoholic KOH (0.1 mol/L).

Polycondensation between Glycolyzed PET and PES (Scheme 2)

The procedure for the polycondensation consisted of adding 5 g of glycolyzed PET, 5 g of PES, and 0.05 g of TTBT in 100 mL equipped with oil bath, thermometer, and a vacuum pump, followed by reacting at 220°C for 1 h. Pressure was kept below 0.1 mmHg. After the reaction was over, the polymeric product was extracted with $CHCl_3$ at 60°C. The $CHCl_3$ solution was filtered and poured dropwise in petroleum ether. After precipitation, the polymer was collected and dried in vacuo at



Scheme 2

70°C for 24 h. On the other hand, the insoluble polymeric product in $CHCl_3$ was dissolved in CF_3COOH. The CF_3COOH solution was filtered and poured in acetone. The precipitate was dried under vacuum at 70°C for 24 h.

The polymer (soluble in $CHCl_3$) film was cast on glass plate and dried at room temperature.

Enzymatic Hydrolysis

Twenty-five milligrams of polymer film and 2 mL of phosphate buffer (KH_2PO_4/Na_2HPO_4, pH 7.0) were placed in a test tube, and the prescribed units of enzyme were added. Blank tests were conducted both for the polymers suspended without enzyme and for the enzyme itself. The enzyme used was a lipase from *Rhizopus arrhizus*. The enzymatic hydrolysis tests were carried out at 37°C for 12 h. After filtration (0.2 μm membrane filter), the total organic carbon (TOC) of the filtrate was measured with a TOC analyzer (Shimadzu TOC500). The net TOC values were calculated by subtracting the average values of the two control tests from the average of two measurements.

Degradation by Activated Sludge

A schematic diagram of the apparatus for an aerobic degradation test was described in detail elsewhere.[23] The supernatant (30 mL, MLSS, 30 mg) of standard activated sludge and a polymer film sample (0.2 g) were placed in a fermentor containing a carbon-free culture medium (500 mL, pH 7.0) according to ASTM D5209-92. The evolved CO_2 was absorbed by a 0.5% hydroxide solution and determined by inorganic carbon concentration (IC) measurement for the alkaline solution with a TOC analyzer at every definite time until the evolution rate reached a plateau. Biodegradation (%) of polymers was calculated by means of the following equation:

$$\text{Biodegradation (\%)} = [(\text{Experimentally measured } CO_2)/(\text{Theoretical } CO_2)] \times 100$$

Theoretically released CO_2 was calculated from the chemical structural formula of these copolymers by assuming that oligomers or monomers, initially formed by enzymatic hydrolysis, were completely mineralized to CO_2.

Analytical Procedures

Characterization of Copolymers

The soluble part in $CHCl_3$ was characterized by GPC (solvent; $CHCl_3$), ^{1}H-NMR (solvent; deuterated chloroform, $CDCl_3$), and DSC. The insoluble part in $CHCl_3$ was characterized by ^{1}H-NMR (solvent; deuterated trifluoro acetic acid, CF_3COOD) and DSC.

Molecular weight (M_n) and molecular weight distributions (M_w/M_n) were determined with GPC (TOSOH, HCL-8020). The columns for GPC measurements were a TSK gel G4000HXL and a TSKgel G3000HXL with limited exclusion molecular weight of 4×10^5. $CHCl_3$ was used as an eluent at a flow rate of 0.6 mL/min. Polystyrene standards with low polydispersities were used to generate a calibration curve. ^{1}H-NMR spectra were recorded on a Varian UNITYplus-400 spectrometer (400 and 100.57 MHz, respectively). All spectra were obtained at room temperature with TMS as an internal standard. DSC measurements were conducted with a TA Instruments DSC2910. The DSC samples varied from 4 to 8 mg, and the heating rate was 10°C/min in the range of temperature from -70 to 200°C. All viscosity measurements were conducted at 30 $\pm$ 0.1°C by employing an Ubbelohde-type viscometer (solvent CF_3COOH).

RESULTS AND DISCUSSION

Glycolysis of PET

A glycolysis reaction of PET is one of the main approaches for the chemical recycling process. In general, EG, PG, and DEG have been used as glycolysis agents taking into account the glycolysis reactivity to obtain monomer unit compounds. In this study, a glycol of higher molecular weight than the above three glycols was used in an attempt to produce a glycolyzed PET having hydroxyl group at both ends (Scheme 1).

GPC traces of the glycolyzed PET with various glycolysis reaction times employing TEEG as glycolysis agent are shown in Figure 1. An increase in the glycolysis reaction time revealed sharp

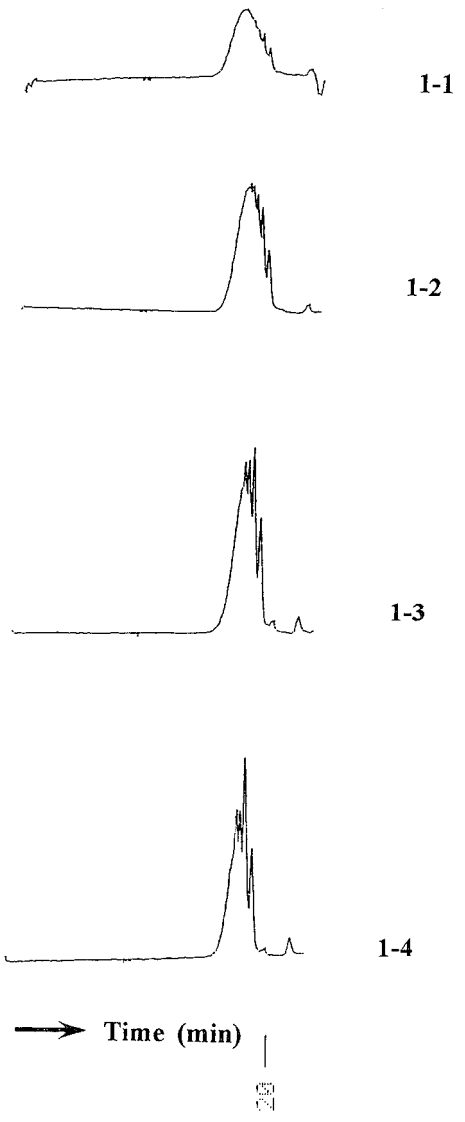


Figure 1 GPC curves of glycolyzed PET products with tetraethylene glycol. 1-1;reaction time 3 h, 1–2; 4.7 h, 1–3; 6.7 h, 1–4; 15 h.

peaks at the low molecular weight region in the GPC curves. This suggests that the resultant glycolysis products are a mixture of compounds of various molecular weights from monomeric units to oligomers, and the glycolysis proceed to monomeric units with an increase in reaction time.

Figure 2 shows the ^{1}H-NMR spectrum of the soluble part in $CHCl_3$ products obtained through PET glycolysis with TEEG. The assignment of ^{1}H-NMR spectra was carried out based on literature data.[24–26] Terephthalyl moiety proton (δ 8.10–8.13 ppm, **s,** 4H, —C_6H_4—) and ethylene oxide proton (δ 4.71 ppm, **s,** 4H, —CH_2CH_2O—) belong to PET. Ethylene oxide proton (δ 3.70–3.74 ppm, **m,** 4H, —CH_2CH_2O—) originate from TEEG, which was used as a glycolysis agent. Moreover, some other detected proton signals (δ 3.99, 4.46–4.52, 3.8–3.90, and 3.60–3.62 ppm) support the formation of new bond after PET glycolysis. The mixtures produced by PET glycolysis reaction consist of compounds having various chemical structures shown in Figure 2.

The results of PET glycolysis reaction are summarized in Table I. The temperature of glycolysis reaction augmented with an increase in molecular weight of glycols. After the glycolysis reaction, the products were dissolved in $CHCl_3$, followed by filtration with filter paper (No. 2). The filtrate was evaporated and washed with methanol to remove nonreactive glycol. The yields in Table I were obtained by calculation on the basis of the amount of the residue after extraction with methanol. The yields were lower than expected because glycolyzed products having low molecular weight were removed through extraction with methanol. The molecular weights of the soluble in $CHCl_3$ glycolyzed products varied within a range from 1100 to 2800. The molecular weight of the glycolyzed products increased with an increase in one of glycol used as a glycolysis agent. The composition, [Terephtalate]/[Glycol] ([TP]/[Gly] mol %) of the glycolyzed products were calculated by integrating the proton signals; aromatic proton (**c**) (δ 8.10–8.13 ppm, **s,** 4H, —C_6H_4—) and methylene proton (**f**) (δ 3.81–3.88 ppm, **m,** 4H, —CH_2CH_2O—) in ^{1}H-NMR spectrum in Figure 2. [TP]/[Gly] moved from 62/38 to 83/17 mol %.

Acid value (AV) and hydroxyl value (HV) of the glycolyzed products have been employed as indicators of polyester decomposition.[9–14,27] AV and HV given in Table I are considerably smaller than those reported by Orbay et al.,[27] who studied the monomer recycling of PET by glycolysis. Because AV values were smaller than HV values, it is reasonable to suggest that the glycolysis reaction proceeds without any side reaction. AV values slightly increased with an increase in reaction time and in the molecular weight of the glycol used as a glycolysis agent. This finding reveals that a side reaction in PET glycolysis occurred when reaction time was prolonged with the rise of reaction temperature. Because AV values were very small, HV values were related to the molecular weight of the glycolyzed products.

The chemical structure of the soluble part in $CHCl_3$ products was investigated on the basis of GPC, DSC, and ^{1}H-NMR spectrometry. From GPC and DSC measurements, the soluble part in

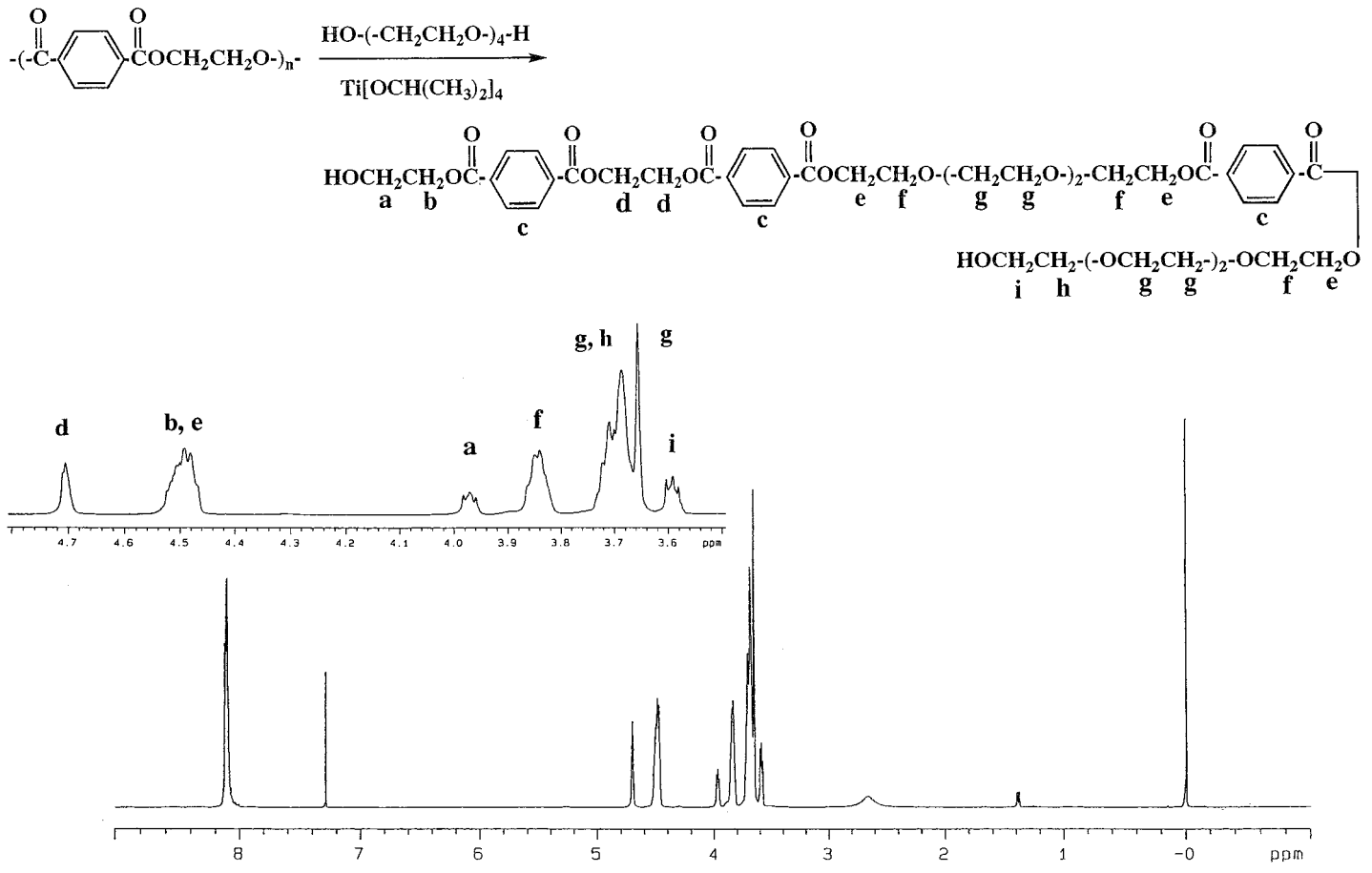


Figure 2 ^{1}H-NMR spectrum of the soluble in $CHCl_3$ glycolyzed PET products with tetraethylene glycol.

Table I Characterization of the Soluble in $CHCl_3$ Part in Glycolyzed PET

	Glycolysis			Glycolyzed PET (Soluble in $CHCl_3$)					
Run	Glycol	Time (h)	Temp. (°C)	Yield (%)	M_n[a]	M_w/M_n[a]	[TP]/[Gly][b] (mol %)	AV[c] (mol/kg)	HV[d] (mol/kg)
1	TEEG	2	200–220	20.7	1120	1.7	67/33	0.05	1.38
2	TEEG	4	200–220	17.0	1210	2.3	71/29	0.05	3.14
3	PEG400	3	230–240	25.7	1610	2.1	67/33	0.05	0.72
4	PEG400	5	230–240	18.1	1380	2.8	69/31	0.17	1.18
5	PTMO650	7	260–270	16.8	2840	2.3	62/38	0.10	0.53
6	PTMO650	16	260–270	35.6	2810	2.1	73/27	0.19	0.30
7	PTMO650	30	260–270	45.0	2200	2.9	68/32	0.19	0.28
8	Pluronic L31	16	260–270	23.0	2300	2.2	83/17	0.11	0.27
9	Pluronic L31	30	260–270	43.3	2700	2.1	81/19	0.16	0.39

[a] From GPC measurement. (solvent; $CHCl_3$, standard; Polystyrene).
[b] [TP]/[Gly] = Molar ratio of [terephthalate]/glycol]. Determined by ^{1}H-NMR analysis. (solvent; $CDCl_3$).
[c] Acid value.
[d] Hydroxyl value.

$CHCl_3$ composed of oligomeric compounds and their molecular weights (M_n) of the glycolyzed PET varied within a range of 1100 to 2800 and no melting points were observed. This shows that the length of terephthalate units in the oligomers was very short. From ^{1}H-NMR measurements it became apparent that the integrated intensities of the methylene peaks linked with terminal hydroxyl group (**a** or **i** in Fig. 2) were smaller than those of the methylene peaks (**c** or **f** in Fig. 2). Therefore, one can propose that the *Oligo*-PET [(2) or (3) in Scheme 1] was produced due to the participation of both terminal hydroxyl groups in the glycolysis reaction.

On the other hand, intrinsic viscosity [η] of the insoluble in $CHCl_3$ glycolyzed products decreased compared to that of the original PET as shown in Table II. Moreover, the melting points of the insoluble in $CHCl_3$ glycolyzed products ranged from about 215 to 250°C, temperatures lower than the original PET. Their melting points decreased with an increase in molecular weight of glycols used as a glycolyzed agent. However, their [η]s was not found to vary with the molecular weights of the glycols. The composition [TP]/[Gly]s ranged from 89/11 to 96/4 mol %. These results suggest the PET lengths of the insoluble part in $CHCl_3$ glycolyzed products were constant regardless of

Table II Characterization of the Insoluble in $CHCl_3$ Part in Glycolyzed PET

	Glycolysis			Glycolyzed PET (Insoluble in $CHCl_3$)			
Run	Glycol	Time (h)	Temp. (°C)	Yield (%)	[η][a] (dL/g)	T_m[b] (°C)	[TP]/[Gly][c] (mol %)
1	TEEG	2	200–220	13.1	0.31	246	92/8
2	TEEG	4	200–220	5.2	0.25	233	89/11
3	PEG400	3	230–240	13.8	0.33	247	95/5
4	PEG400	5	230–240	22.1	0.28	247	94/6
5	PTMO650	7	260–270	30.0	0.28	246	95/5
6	PTMO650	16	260–270	8.6	0.25	227	90/10
7	PTMO650	30	260–270	15.6	0.25	238	95/5
8	Pluronic L31	16	260–270	60.0	0.24	215	94/6
9	Pluronic L31	30	260–270	50.0	0.17	217	96/4

[a] Determined by viscosity measurement at 30°C.
[b] From DSC measurement.
[c] [TP]/[Gly] = Molar ratio of [terephthalate]/[glycol]. Determined by ^{1}H-NMR analysis. (solvent; CF_3COOD).

Table III Enzymatic Hydrolyzability of PET Glycolyzed Products

Run	Glycolysis: Glycol	Glycolysis: Time (h)	Glycolysis: Temp. (°C)	Enzymatic hydrolyzability (TOC/ppm): Soluble in $CHCl_3$ Part: A[a]	Soluble in $CHCl_3$ Part: B[b]	Insoluble in $CHCl_3$ Part: A[a]	Insoluble in $CHCl_3$ Part: B[b]
1[c]	TEEG	2	200–220	760 (180)	10 (10)	240	<5
2	TEEG	4	200–220	260	10	90	<5
3[c]	PEG400	3	230–240	750 (570)	30 (30)	150	<5
4	PEG400	5	230–240	630	<5	130	5
5	PTMO650	7	260–270	60	<5	50	10
6[c]	PTMO650	16	260–270	60 (20)	20 (10)	30	<5
7	PTMO650	30	260–270	50	5	220	10
8[c]	Pluronic L31	16	260–270	250 (110)	<5 (90)	50	<5
9	Pluronic L31	30	260–270	400	<5	70	<5

[a] A; Total organic carbon (ppm) of water-soluble compound produced without lipase.
[b] B = TOC value of water-soluble compound produced with lipase − A value.
[c] TOC in parentheses show the value measured using the samples after extraction with buffer solution at 37°C for 24 h.

the structures of the glycols. However, the melting points changed with the type of glycols linked at the end of the glycolyzed products.

Enzymatic Hydrolyzabilities of the Glycolyzed Products

The results of enzymatic hydrolysis with a lipase of the glycolyzed products are summarized in Table III. The TOC values of the glycolyzed products in control experiments in the absence of enzyme were high except PTMO650 (runs 5, 6, and 7). In an attempt to get an insight into these results, the relationship of TOC, in the absence of enzyme, with immersion time was investigated. Some representative results are shown in Figure 2. All TOC values leveled off within 6 h. This indicates that the glycolyzed products other than PTMO650 contain a large amount of the water-soluble compounds. All TOC values, in the presence of an enzyme, of the soluble part in $CHCl_3$ glycolyzed products were very small. This means that the glycolyzed products are not hydrolyzed with a lipase from *Rhizopus arrhizus*. Four typical glycolyzed products were hydrolyzed with or without a lipase after extraction with buffer solution used in the enzymatic hydrolysis at 37°C for 24 h. The results are summarized in parentheses in Table III. From these observations, it was confirmed that the glycolyzed PET was not hydrolyzed with lipase. However, in the case of the glycolyzed PET products with Pluronic L31, the TOC values measured in the presence of lipase following extraction with the phosphate buffer solution were higher than the one measured prior to extraction. Moreover, the TOC values measured in the absence of the lipase were low. These results prove that the glycolyzed PET with Pluronic L31 are hydrolyzed by the lipase.

Polycondensation of the Glycolyzed Products with PES

The results of polycondensation of the glycolyzed PET with PES are shown in Table IV. The molecular weights (M_n) of PES used ranged from 7000 to 11,000, and the composition [SA]/[EO] was 48/52 mol %. The copolymer yields varied from 67 to 90 wt %. Their M_ns varied within a range from 10,000 to 24,000.

The M_ns of the copolymers prepared from the soluble part in $CHCl_3$-glycolyzed products were lower than those of the copolymers synthesized from the insoluble part in $CHCl_3$-glycolyzed products. The composition, [TP]/[SA], of the copolymers prepared from the soluble part in $CHCl_3$ glycolyzed part ranged from 21/79 to 45/55 mol %. On the other hand, in the case of the copolymers prepared from the insoluble part in $CHCl_3$, phthalate moiety-rich copolymers were produced.

DSC measurements of the copolymers obtained disclosed the melting points of the various copolymers (runs 3, 4, 5, and 8). The copolymers prepared from the soluble part in $CHCl_3$ products

Table IV Results of Polycondensation of Glycolyzed PET and Copoly(succinic anhydride/ethylene oxide)(PES)

	Glycolyzed PET		Copolymer						
Run	Glycol	Solubility in $CHCl_3$	Yield (%)	M_n	M_w/M_n	[TP]/[SA][a] (mol %)	T_m (°C)	ΔH (J/g)	T_g (°C)
10	TEEG	soluble	78	17,600	1.9	36/64	—	—	−29
11	TEEG	insoluble	79	23,900	1.9	39/61	—	—	1
12	PEG400	soluble	89	10,600	2.7	21/79	58	9.0	−28
13	PEG400	insoluble	80	20,500	2.5	40/60	134	0.5	−16, 50
14	PTMO650	soluble	75	14,700	2.4	25/75	62, 86	16.5	−21
15	PTMO650	insoluble	75	18,500	2.0	45/55	—	—	2
16	Pluronic L31	soluble	81	10,700	2.1	25/75	61, 81	13.4	−19
17	Pluronic L31	insoluble	67	22,400	2.1	63/37	—	—	−11, 42

[a] [TP]/[SA] = Molar ratio of [terephthalate unit]/[succinate unit] was determined by ^{1}H-NMR analysis.

(runs 3, 5, and 8) with a T_m of about 60°C were derived from various PES length units. Moreover, the ΔHs at the melting point of these copolymers were shown to be greater than the run 4 copolymer of a T_m (= 134°C) derived from the PET length.

The T_gs of the copolymers prepared from the soluble part in $CHCl_3$ products (runs 1, 3, 5, and 8) ranged from −29 to −19°C. The T_gs of the copolymers prepared from the insoluble part in $CHCl_3$ products (runs 2, 4, 6, and 8) were determined within a wide range of temperatures. The results from thermal properties in conjunction with the composition [TP]/[SA] suggest that the T_gs of the PES-rich copolymers prepared from the soluble part in $CHCl_3$ came from the PES length. On the other hand, the T_gs of the PET-rich copolymers prepared from the insoluble part in $CHCl_3$ were closely related to the PET length. The random copolymers were produced under transesterification conditions, and the T_gs were located at the temperature between the T_gs of the stating materials.

Hydrolyzabilities with Lipase or Activated Sludge

The results of hydrolysis of the copolymers prepared the glycolyzed products with PES with the lipase or activated sludge are summarized in Table V. The hydrolyzabilities of the glycolyzed products were low, as previously described (in Table III). Moreover, the hydrolyzability with a

Table V Results of Enzymatic Hydrolysis and Biodegradation by Activated Sludge of Copolymers Synthesized by Polycondensation between Glycolyzed PET and PES

	Glycolyzed PET		Enzymatic Hydrolyzability			Biodegrad. by Activated Sludge (wt %)					
Run	Glycol	Solubility in $CHCl_3$	TOC-A[a] (ppm)	TOC-B[b] (ppm)	Degrad. (wt %)	7 Days	14 Days	21 Days	28 Days	35 Days	58 Days
10	TEEG	soluble	100	760	10.9	—	—	—	—	—	—
11	TEEG	insoluble	110	310	4.4	0.5	0.5	1.7	6.5	10.7	—
12	PEG400	soluble	230	100	1.4	—	—	—	—	—	—
13	PEG400	insoluble	180	510	7.3	0	0.4	0.4	2.0	—	—
14	PTMO650	soluble	150	780	11.1	—	—	—	—	—	—
15	PTMO650	insoluble	80	150	2.1	0.4	3.2	3.9	4.7	—	—
16	Pluronic L31	soluble	110	200	2.9	—	—	—	—	—	—
17	Pluronic L31	insoluble	160	730	10.3	5.9	6.3	6.7	7.0	7.0	12.1

[a] Total organic carbon of water-soluble compounds without lipase.
[b] Lipase from *Rhizopus arrhizus* (1250 U) was used. TOC value = (TOC with lipase) − (TOC without lipase).

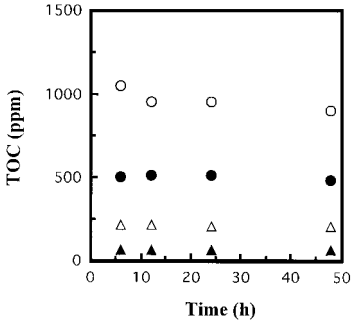


Figure 3 Solubilities of glycolyzed PET in phosphate buffer solution (pH 7.0). (○); PET glycolyzed with polyethylene glycol 400, (●); with tetraethylene glycol, (△); with Pluronic L31, (▲); with polytetramethylene oxide 650.

lipase of PES having [SA]/[EO] composition 48/52 mol % was equally low, as reported in a previous article.[19] The TOC value with the lipase from *Rhizopus arrhizus* was below 20 ppm. Meanwhile, the enzymatic hydrolyzabilities of the resultant copolymers were higher than those of both starting materials. The enzymatic hydrolyzabilities of the copolymers prepared from the soluble part in $CHCl_3$-glycolyzed products were higher than those of the copolymers synthesized from the insoluble part in $CHCl_3$-glycolyzed products using TEEG (runs 10 and 11) and PTMO650 (runs 14 and 15). However, this tendency was reversed in the case of PEG400 (runs 12 and 13) and Pluronic L31 (runs 16 and 17).

In connection with these results, one could speculate that another transreaction, such as transesterification between the PET glycolyzed products and PES, proceeds in the polycondensation.[28] As a result of this transreaction, a random biodegradable copolymer is produced. Moreover, the biodegradabilities of the resultant polymers are substantially affected by the degree of this transreaction.

Biodegradabilities of the copolymers prepared from the insoluble part in $CHCl_3$-glycolyzed products were studied in the presence of an activated sludge. An induction period is often observed in a biodegradation test using an activated sludge.[29] Biodegradation of the copolymers prepared from the glycolyzed PET using TEEG or PEG400 was initiated over 20 days, whereas from PTMO650 it was over 7 days. Moreover, one from Pluronic L31 was initiated simultaneously with the beginning of the biodegradation test. Biodegradation of these copolymers was lower than that of popular biodegradable polymers such as poly(butylene succinate)[17] and poly(ε-caprolactone).[17]

CONCLUSIONS

PET was glycolyzed by various glycols in the presence of TIP as a catalyst. The M_ns of the soluble part in $CHCl_3$ in the glycolyzed PET ranged from 1100 to 2900, and no melting points were observed. The insoluble part in $CHCl_3$ in the glycolyzed PET had a melting point varying from 215 to 250°C.

In the polycondensation of the glycolyzed PET and PES, a transesterification occurred and a random copolymer was obtained on several occasions. The hydrolyzabilities of the copolymers containing a PET length in the presence of a lipase or activated sludge increased compared to those of the starting materials. The glycolyzed PET has a reactive hydroxyl group at the terminal groups. The glycolyzed PET can be used as a useful raw material to synthesize a polyester, copolyesterether, and polyurethane.

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