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Study of the glycolysis of PET by oligoesters

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Abstract

A series of oligoesters was synthesized via the transesterification of dimethyl isophthalate with neopentyl glycol or tetraethylene glycol and the esterification of adipic acid with neopentyl glycol or tetraethylene glycol under diol/diester or diol/diacid molar ratios sufficient to limit molecular weight increasing.

These oligoesters were used to depolymerize poly(ethylene terephthalate) (PET) in the presence of zinc acetate to yield new types of glycolysates. The oligoesters and the glycolysates are characterized by ^{1}H NMR, size exclusion chromatography (SEC), differential scanning calorimetry (DSC), thermogravimetric analyses and matrix assisted laser desorption/ionisation time of flight mass spectrometry (MALDI-TOF MS). These analyses revealed the structure of the different glycolysates.

Keywords: Glycolysis; PET; Oligoester

1. Introduction

Polyethylene terephthalate (PET) is a worldwide used polymer, and packaging is one of its most important applications. Due to its high resistance to the atmospheric and biological agents, this polymer is not considered as biodegradable. PET is not a hazardous product, but its waste quantity increases drastically and so it is a good candidate for recycling. PET waste can be recycled by different methods like physical recycling and chemical recycling. Physical recycling consists in grinding, washing and extruding of PET waste and in reusing in production or in applications like textile. But PET waste is a mixture of charges and other polymers than PET, so this inhomogeneous blend has not the same properties as virgin PET. Chemical recycling is the reaction of PET with various reagents to obtain products that are used in the chemical industry. Different ways, based on the reactivity of ester-bond were explored, only few have been developed at an industrial scale.

The most studied chemical recycling way consists of the reaction between PET and a monoalcohol or a diol. The methanolysis consists in the depolymerization of PET by methanol and yields a precursor of PET [1–3].

In a similar way, simple glycolysis is the reaction of depolymerization of PET with ethylene glycol (EG) [4–9] leading to bis hydroxy ethyl terephthalate (BHET) and PET oligomers. However, the resulting glycolysate is very crystallized. Diethylene glycol (DEG) was the second most studied diol for glycolysis [2,8,10–26]. The resulting oligomers contain two diol segments—one derived from the diol and the second one derived from EG—and storage problems appear [10,27–30].

If the glycolysis of PET with only one diol is well-known, the glycolysis of PET by a mixture of diols has also been investigated [31–33]. In this paper, we describe an attempt to limit the crystallization in order to improve storage properties.

The glycolysis of PET was achieved with an oligomer of a polyester named oligoester. The oligoester was synthesized by reaction of one acid segment and two diol segments. Of course, the reaction of diacid and diol causes molecular weight increase but Diakoumakos et al. [34]

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explains how to limit it, that is why we talk about oligoester and not about diester. Polyester properties are due to the combination of diol segments and diacid segments. The choice of the diacid and diol segments is based on the improvement of the properties of the glycolysate and the lower cost of the raw materials.

Two diol and two diacid segments were chosen and we studied their influences on the properties of the glycolysates. Adipic acid is well-known to improve flexibility of polyester, and the introduction of isophthalate core in terephthalic based glycolysate could decrease the crystallinity.

2. Experimental

2.1. Materials

Polyethylene terephthalate (PET) (T74F9) was purchased from Tergal Fibre company (Gauchy, France) in the form of pellets: its melting point was about 252 °C and its density about 1.40 g/cm^{-3}.

Adipic acid, dimethyl isophthalate, neopentyl glycol, oxalic acid, potassium hydroxide, tetraethylene glycol, zinc acetate dihydrate, ethanol from Sigma-Aldrich (St Quentin Fallavier, France) were analytical grade and were used without further purification.

2.2. Instrumentation

IR spectra were recorded on a Nicolet (Madison, WI) 510P Fourier Transform InfraRed (FTIR) spectrometer.

NMR spectra were recorded on a Bruker (Wissembourg, France) AC200 (200 MHz) or Avance250 spectrometer (250 MHz) with tetramethylsilane as the reference for ^{1}H-NMR. The chemical shifts are reported in part per million, where s is a singlet; d, a doublet; t, a triplet; and m, a multiplet. Unless otherwise specified, all of the spectra were recorded from $CDCl_3$ solutions.

Differential scanning calorimetry (DSC) analyses were performed under nitrogen with a Perkin–Elmer (Paris, France) Pyris 1 DSC apparatus calibrated with *n*-octane and indium. All of the samples were heated from −120 to 180 °C at 20 °C/min; three runs were recorded, and the glass-transition temperature (T_g) values were measured during the second run and confirmed by the third one. They were calculated at the half height of the heat capacity jump of the glass transition.

Thermogravimetric analyses were performed in nitrogen on a TGA 51 from TA Instruments(Guyancourt, France) at a heating rate of 10 °C/min from 50 to 700 °C.

Size exclusion chromatography (SEC) was performed on a Spectra Physics apparatus with two PL gel columns (5 μm particle size, 30 nm length, and 50 Å and 100 Å pore size) and one Styragel HR2 column (7.8 mm internal diameter and 300 mm length). The samples were injected via an automatic injector SIL 10A of Shimadzu. The detection was achieved with a SP8430 differential refractometer. The eluent was tetrahydrofurane (THF), with a flow of 0.8 mL.min^{-1}.

The products were analyzed by matrix-assisted laser desorption ionisation time of flight (MALDI-TOF). The spectra were recorded in linear mode on a Voyager DE-STR (Applied Biosystem) spectrometer equipped with a 337 nm nitrogen laser. 1,8,9 trihydroxyanthracene (Dithranol) with a concentration of 10 g/l in 1,1,1,6,6,6-hexafluoroisopropanol (HFIP) was used as matrix. The samples were dissolved in HFIP (10 g/l) and added to the matrix in a ratio matrix-sample-NaI (10/1/1, v/v/v). 1 μl of this mixture was deposited on the target. Na^+ is the cationising agent.

The acid value (I_a) is the number of milligrams of potassium hydroxide necessary to neutralize the acid functions present in one gram of polyester. The sample was dissolved in a mixture of 20 ml of THF and 4 ml of water then this solution was titrated by a solution of potassium hydroxide (0.83 N KOH-ethanol solution). The indicator used during this titration was Bromothymol Blue. The acid value was calculated according to Eq. (1):

$$I_a = \frac{56,1(V_1 - V_0)T}{m} \quad (1)$$

where, V_0, volume in millilitres of the solution of potassium hydroxide used during the blank test (without sample); V_1, volume in millilitres of the solution of potassium hydroxide used during the test; m, mass in grams of the sample used; T, titre of the solution of potassium hydroxide used (in mol/l)

The hydroxyl values were determined following the standard method NF T 52-113. This method is briefly described as follows. About 0.5 g of the sample was accurately weighed and added to 20 ml of acetylating solution containing 1000:127 (v/v) pyridine and acetic anhydride, in a 50 ml round-bottomed flask. The flask equipped with a condenser and magnetic stirrer was heated at 100 °C for about 2 h. The mixture was cooled at room temperature and added, in another flask, to 100 ml of water. Under vigorous stirring, the resulting solution was titrated with a 0.5 N NaOH standard using phenolphthalein as indicator. A blank run, without the sample, was also performed.

$$I_{OH} = \frac{56.1(V_0 - V_1)T}{m} + I_a$$

where, V_0, volume in millilitres of the NaOH standard solution used for the blank test (without sample); V_1, volume in millilitres of the NaOH standard solution used for the test with sample); m, mass in grams of the sample; T, concentration of NaOH standard solution; I_a, acid value (in mg KOH/g).

2.3. Synthesis of oligoesters

2.3.1. Synthesis of the oligoester A

Adipic acid (37.6 g, 0.257 mol), neopentyl glycol (75 g, 0.720 mol) and zinc acetate dihydrate (0.5 g, 1.3% w/w in respect to adipic acid weight) were charged into a two-necked

250 ml round-bottomed flask equipped with a Dean-Stark trap, a magnetic stirrer and a condenser. The mixture was heated at 140 °C during 3 h while collecting water in the Dean-Stark trap. When visible water collection ended, the mixture was maintained at 140 °C for 3 h. After cooling, the product became a white crystalline paste.

$M_n = 747$, $M_w = 810$, $M_z = 897$. Acid value = 33 mg KOH/g, hydroxyl value = 403 mg KOH/g. $T_g = -67$ °C. FT-IR (cm^{-1}): 3427 (O–H stretching); 1726 (C=O).

^1H NMR ($CDCl_3$) δ: 3.92–3.86 (d, $–CH_2–$ protons of the neopentyl glycol in a α-position to –O–C=O); 3.50–3.29 (m, $–CH_2–$ protons of neopentyl glycol segment in α-position to –OH); 2.65 (s, hydroxyl protons of the neopentyl glycol); 2.36 (m, $–CH_2–$ protons of adipic acid segment in α-position to O=C); 1.67 (m, $–CH_2–$ protons of adipic acid segment in β-position to O=C); 0.95–0.9 (multiplet, $–CH_3$ protons of the neopentyl glycol).

2.3.2. Synthesis of the oligoester B

A similar procedure as for the synthesis of oligoester A was used. Adipic acid (18.8 g, 0.128 mol) tetraethylene glycol (70 g, 0.360 mol) and zinc acetate dihydrate (0.25 g, 1.3% w/w in respect to adipic acid weight) were reacted. After cooling, the product was a transparent liquid.

$M_n = 838$, $M_w = 913$, $M_z = 1018$. Acid value = 47 mg KOH/g, hydroxyl value = 341 mg KOH/g. $T_g = -70.27$ °C. FT-IR (cm^{-1}): 3370 (O–H stretching); 1731 (C=O).

^1H NMR ($CDCl_3$) δ: 4.22 (t, $–CH_2–$ protons of the tetraethylene glycol segment in α-position to –O–C=O); 3.67 (m, $–CH_2–$ protons of tetraethylene glycol); 3.23 (s, hydroxyl protons of the tetraethylene glycol); 2.35 (m, $–CH_2–$ protons of adipic acid segment in α-position to O=C); 1.65 (m, $–CH_2–$ protons of adipic acid segment in β-position to O=C).

2.3.3. Synthesis of the oligoester C

A similar procedure as for the synthesis of oligoester A was used. Dimethyl isophthalate (50 g, 0.258 mol), neopentyl glycol (75 g, 0.720 mol) and zinc acetate dihydrate (0.5 g, 1% w/w in respect to dimethyl isophthalate weight) were reacted. When visible methanol collection ended, the mixture was maintained at 140 °C for 3 h. After cooling, the product became a white crystalline paste.

$M_n = 696$, $M_w = 759$, $M_z = 841$. Acid value = 2 mg KOH/g, hydroxyl value = 442 mg KOH/g. T_g = -21.6 °C. FT-IR (cm^{-1}): 3428 (O–H stretching); 1725 (C=O); 1609 (benzene ring).

^1H NMR ($CDCl_3$) δ: 8.64 (d, aromatic proton in ortho-position to one C=O subtituent and meta-position to the other C=O substituent); 8.22 (m, aromatic protons in ortho-position to each C=O); 7.55(m, aromatic proton in meta-position to each C=O); 4.28–4.21 (m, $–CH_2–$ protons of neopentyl glycol in α-position to –O–C=O); 3.95 (s, $O–CH_3$); 3.51–3.41 (m, $–CH_2–$ protons of neopentyl glycol in α-position to –OH); 2.19 (s, hydroxyl protons of neopentyl glycol); 1.18–0.91 (multiplet, $–CH_3$ protons of neopentyl glycol).

2.3.4. Synthesis of the oligoester D

A similar procedure as for the synthesis of oligoester C was used. Dimethyl isophthalate (25.25 g, 0.130 mol), tetraethylene glycol (69.95 g, 0.360 mol) and zinc acetate dihydrate (0.25 g, 1% w/w in respect to dimethyl isophthalate weight) were reacted. After cooling, the product stayed a transparent liquid.

$M_n = 656$, $M_w = 704$, $M_z = 767$. Acid value = 3 mg KOH/g, hydroxyl value = 331 mg KOH/g. $T_g = -69.8$ °C. FT-IR (cm^{-1}): 3368 (O–H stretching); 1725 (C=O); 1609 (benzene ring).

^1H NMR ($CDCl_3$) δ: 8.68 (s, aromatic proton in ortho-position to one C=O subtituent and meta-position to the other C=O substituent); 8.23 (m, aromatic protons in ortho-position to each C=O substituents); 7.52 (t, aromatic proton in meta-position to each C=O substituents); 4.5 (t, $–CH_2–$ protons of the tetraethylene glycol in α-position to –O–C=O substituent); 3.93 (s, $O–CH_3$); 3.85–3.46 (m, $–CH_2–$ protons of tetraethylene glycol; 3.14 (s, hydroxyl protons of the tetraethylene glycol).

2.4. Synthesis of glycolysates

2.4.1. Synthesis of PETA

PET pellets (20.03 g: 0.104 mol (PET monomer unit)), oligoester A (34.74 g: 0.209 mol of hydroxyl equivalent), and 0.20 g of zinc acetate (ZnAc) were put into a 500 ml reactor equipped with a mechanic stirrer, a nitrogen inlet and a vacuum outlet. The reactor was heated under nitrogen at 240 °C for 2 h. The mixture was cooled 5 min and EG vapor was eliminated under reduced pressure (18 mmHg) during 5 min. The cooled product appeared as a translucent and viscous liquid.

$M_n = 1057$, $M_w = 1341$, $M_z = 1744$. Acid value = 3 mg KOH/g, hydroxyl value = 274 mg KOH/g. $T_g = -34$ °C.

^1H NMR ($CDCl_3$) δ: 8.1 (d, aromatic proton between the C=O groups);4.70 (t, $–CH_2–$ protons of the ethylene glycol between two terephthalic segments); 4.26–4.14 (t, $–CH_2–$ protons of the ethylene glycol); 3.98–3.86 (t, $–CH_2–$ protons of the neopentyl glycol in a α-position to –O–C=O); 3.73(s); 3.51–3.29 (s, $–CH_2–$ protons of neopentyl glycol segment in α-position to –OH); 2.34 (s, $–CH_2–$ protons of adipic acid segment carbon atom in a α-position to O=C); 1.64 (s, $–CH_2–$ protons of adipic acid segment carbon atom in a β-position to O=C); 1.170–0.90 (m, $–CH_3$ protons of the neopentyl glycol).

2.4.2. Synthesis of PETB

A similar procedure as for the synthesis of PETA was used. PET pellets (20.00 g: 0.104 mol (PET monomer unit)), oligoester B (47.64 g: 0.210 mol of hydroxyl equivalent), and 0.21 g of zinc acetate (ZnAc) were put in

reaction. The cooled product appeared as a translucent and viscous liquid.

M_n = 1348, M_w = 1853, M_z = 2651. Acid value = 4 mg KOH/g, hydroxyl value = 204 mg KOH/g. T_g = −52.4 °C

^{1}H NMR ($CDCl_3$) δ: 8.10 (s, aromatic proton of terephthalic segment); 4.69 (s, –CH_2– protons of the ethylene glycol between two terephthalic segments), 4.47(t, –CH_2– protons of the ethylene glycol); 4.20 (s, –CH_2– protons of the tetraethylene glycol atom in α-position to –O–C=O); 3.81 (s, –CH_2– in α-position to OH in TEG segment); 3.64 (m, –CH_2– protons of tetraethylene glycol), 2.59 (s, hydroxyl protons), 2.33 (s, –CH_2– protons of adipic acid in α-position to O=C), 1.63 (s, –CH_2– protons of adipic acid in β-position to O=C).

2.4.3. Synthesis of PETC

A similar procedure as for the synthesis of PETA was used. PET pellets (20.07 g: 0.104 mol (PET monomer unit)), oligoester C (26.73 g: 0.209 mol of hydroxyl equivalent), and 0.23 g of zinc acetate (ZnAc) were put in reaction. The cooled product appeared as a transparent and very viscous liquid.

M_n = 1179, M_w = 1589, M_z = 2202. Acid value = 4 mg KOH/g, hydroxyl value = 199 mg KOH/g. T_g = 5.68 °C.

^{1}H NMR ($CDCl_3$) δ: 8.64 (s, aromatic proton of isophthalate segment in ortho position to one C=O subtituent and meta position to the other C=O substituent); 8.19 (m, aromatic protons in ortho position to each C=O of isophthalate segment); 8.06 (m, aromatic protons in terephthalate segment); 7.50 (t, aromatic proton in meta-position to each C=O substituent of isophthalate segment); 4.68 (s, –CH_2– protons of the ethylene glycol between two terephthalic segments); 4.47 (m, –CH_2– protons of the ethylene glycol); 4.25–4.18 (m, –CH_2– protons of the neopentyl glycol in α-position to –O–C=O);3.721; 3.49–3.39 (m, –CH_2– protons of neopentyl glycol in α-position to –OH) 2.45 (s, hydroxyl protons); 1.16–0.89 (multiplet, –CH_3 protons of the neopentyl glycol).

2.4.4. Synthesis of PETD

A similar procedure as for the synthesis of PETA was used. PET pellets (20.00 g: 0.104 mol (PET monomer unit)), oligoester D (35.90 g: 0.208 mol of hydroxyl equivalent), and 0.20 g of zinc acetate (ZnAc) were put in reaction. The cooled product appeared as a translucent and viscous liquid.

M_n = 1324, M_w = 1858, M_z = 2660. Acid value = 3 mg KOH/g, hydroxyl value = 143 mg KOH/g. T_g = −28 °C.

^{1}H NMR ($CDCl_3$) δ: 8.68 (s, aromatic proton of isophthalate segment in ortho-position to one C=O subtituent and meta-position to the other C=O substituent); 8.23 (m, aromatic protons in ortho-position to each C=O substituent of isophthalate segment); 8.08 (m, aromatic protons in terephthalate segment); 7.50 (t, aromatic proton in meta-position to each C=O of isophthalate segment); 4.68(s, –CH_2– protons of the ethylene glycol between two terephthalic segments); 4.46 (t, –CH_2– protons of the tetraethylene glycol in α-position to –O–C=O); 3.93 (s, O–CH_3); 3.81–3.66 (m, –CH_2– protons of tetraethylene glycol; 3.14 (s, hydroxyl protons of the tetraethylene glycol); 2.46 (s, hydroxyl protons).

After cooling, the different glycolysates seemed not to evolve during at least 6 months.

3. Results and discussion

3.1. Synthesis of oligoesters and glycolysates

The same catalyst as that used for the glycolysis step was reacted for the synthesis of the oligoesters to avoid the interactions between catalysts likely to distort the observations.

Adipic acid, dimethyl isophthalate, tetraethylene glycol (TEG) were chosen to decrease crystallinity and viscosity, and neopentyl glycol was selected with the target to reduce the crystallinity of the glycolysates.

The condensation of the diacids with the diols was achieved with a sufficient molar ratio to limit the rise in molecular weight according to Diakoumakos [34]. The expected products were diesters usable for glycolysis of PET. For that, the molar ratio diol/diacid = 2.8 was used. Reactions were performed between the different diacids and diols and the structures of the products are summed up in Table 1. Even if free diols were noticed, SEC chromatograms showed a slight rise in molecular weight despite the fact that the expected product was the main compound (the diester with one diacid segment and two diol segments). The free diols are usefull for the glycolysis because they are

Table 1
Structure of the attempted diesters synthesized

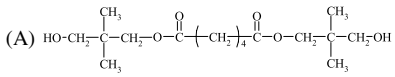
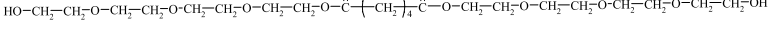
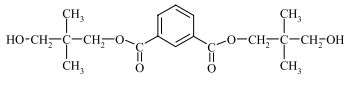
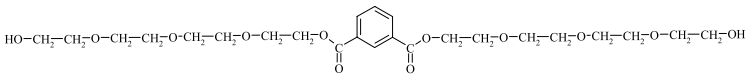
Acid\diol	Neopentyl glycol	Tetraethylene glycol
Adipic acid	(A) 	(B) 
Dimethyl isophthalate	(C) 	(D) 

Table 2
Characteristics of hydroxyl terminated oligoesters (M_n determined by SEC with PS-standards)

Product	Theoretical molecular weight of principal product (g/mol)	Experimental $\bar{M}_n$ SEC	Ip	Hydroxyl value in mg KOH.g^{-1}	Acid value in mg KOH.g^{-1}	%mol of acid % Acid = $\frac{CO_2H}{CO_2H+OH}$	Apparent molecular weight in g.mol^{-1}
A	318.4	747	1.08	403	33	8	277
B	498.6	838	1.09	341	47	15	329
C	338.4	696	1.09	442	2	<1	254
D	518.6	656	1.07	331	3	<1	339

Table 3
Hydroxyl values and acid values of the glycolysates and calculated molecular weight of the obtained diols (hydroxyl terminated glycolysate)

Glycolysate	Hydroxyl value in mg KOH g^{-1}	Acid value in mg KOH g^{-1}	%mol of acid % Acid = $\frac{CO_2H}{CO_2H+OH}$	Molecular weight of equivalent diol in g mol^{-1}
PET + A	274	3	1	409
PET + B	204	4	2	551
PET + C	199	4	2	562
PET + D	143	3	2	785

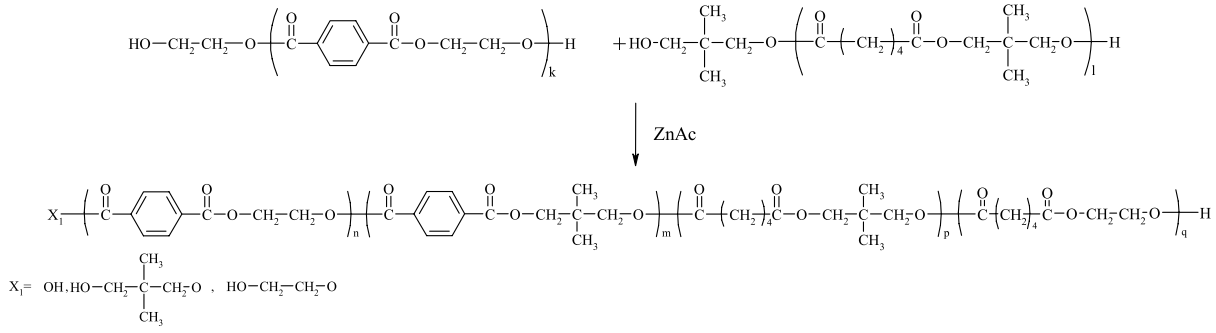
Table 4
Comparison between the introduced acid amount present in the oligoester before glycolysis and the residual acid amount after glycolysis

Oligoester	Molar acid function content introduced before glycolysis	Glycolysate	Number of mol of final acid after glycolysis (10^{-3})
A	2.029×10^{-2}	PET + A	3.32
B	3.962×10^{-2}	PET + B	4.37
C	8.6×10^{-4}	PET + C	3.48
D	1.76×10^{-3}	PET + D	2.87

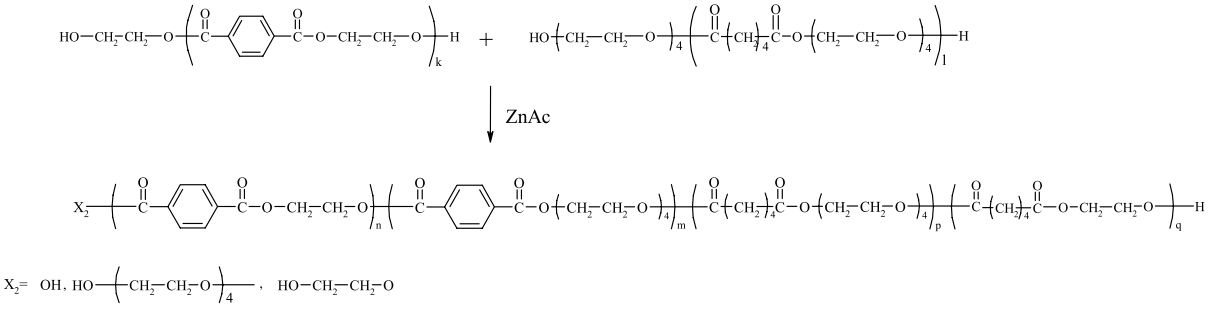
Molar acid function content introduced before glycolysis = number of mol of introduced acid = acid value of the oligoester (mol g^{-1})* mass of oligoester introduced for glycolysis number of mol of final acid after glycolysis = acid value of the glycolysate (mol g^{-1})* mass of the glycolysate.

more movable and reactive than the oligoesters. So they facilitate the PET depolymerization starting. The compounds were analyzed by SEC (Table 2) with PS standards and results are only indicative values considering we had not the Mark–Houwink coefficients of these types of compounds. The hydroxyl and acid values of the product obtained were measured. Indeed, the product was a mixture of OH terminated polyesters. A Maldi-TOF study of these oligoesters was achieved to characterize qualitatively the various compounds of this mixture. To have a coherent procedure, the index of hydroxyl (corrected by the acid value if this one was too large) have been measured and used for calculation of the diol content to introduce for the glycolysis of the PET (Table 2). To simplify, two moles of hydroxyl functions were used for one mole of PET unit.

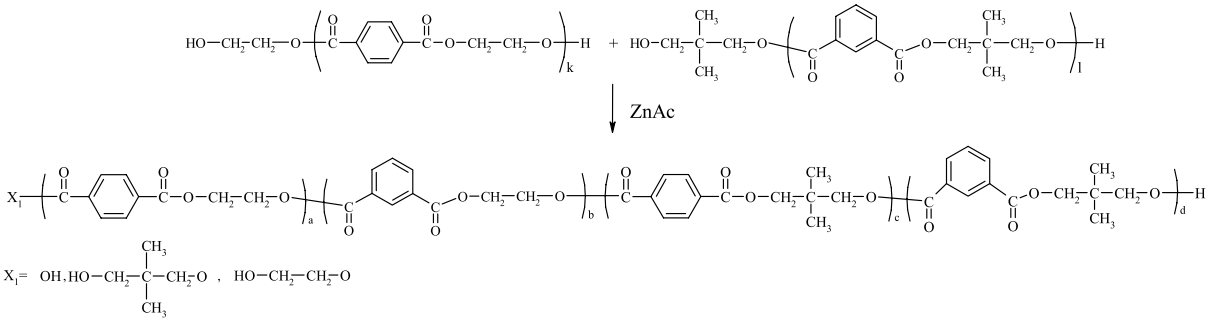
Two types of diacids and two different diols were used in order to obtain four oligoester structures likely to be used for the glycolysis of the PET. Instead of a mixture of diol and diacid, the oligoesters are interesting in the glycolysis in



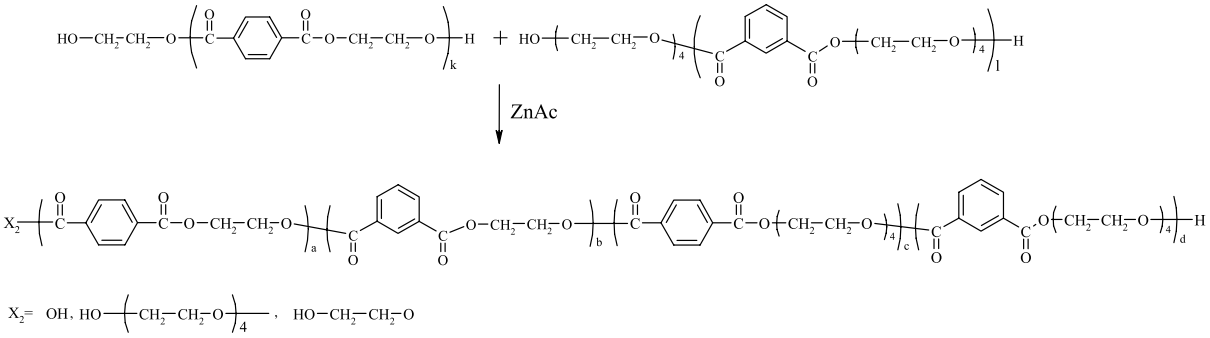
Scheme 1. Glycolysis of PET by oligoester A.



Scheme 2. Glycolysis of PET by oligoester B.



Scheme 3. Glycolysis of PET by oligoester C.



Scheme 4. Glycolysis of PET by oligoester D.

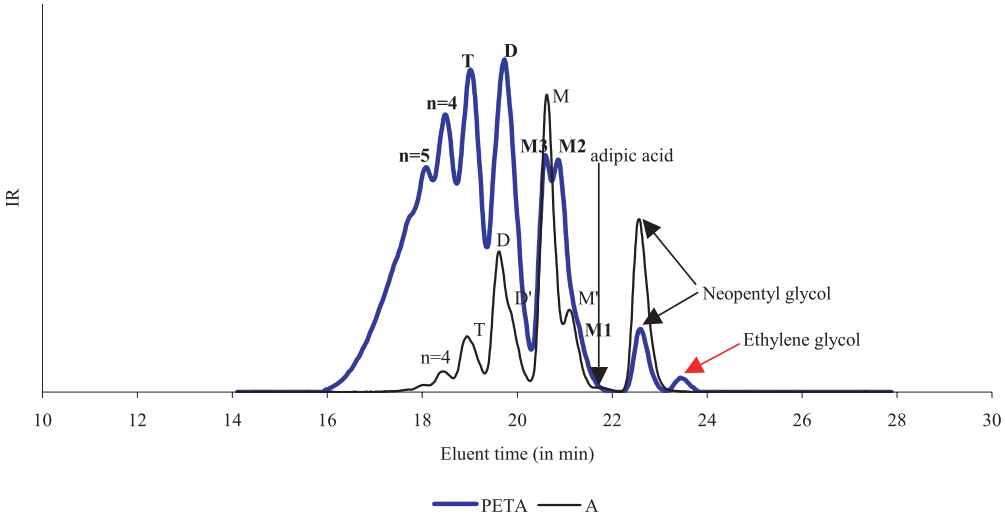


Fig. 1. SEC comparison of oligoester A and PETA.

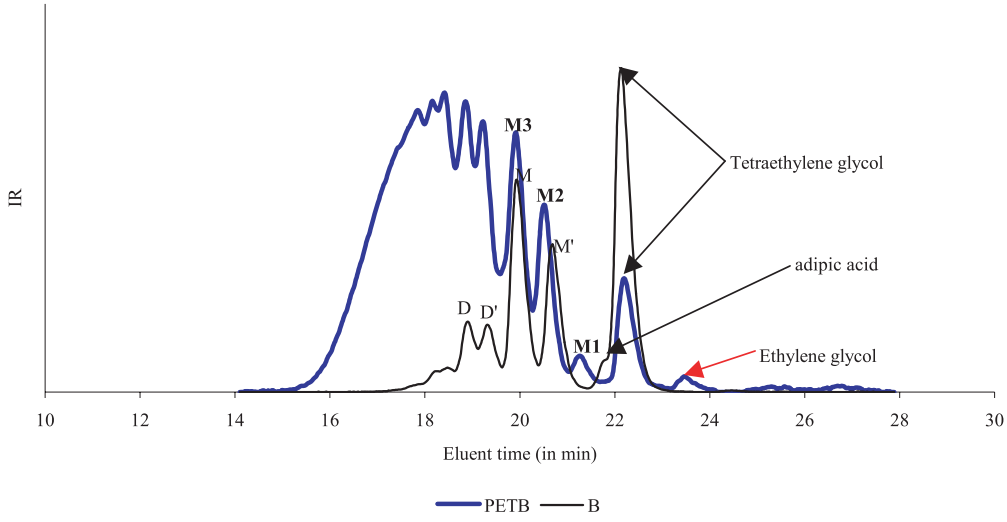


Fig. 2. SEC comparison of oligoester B and PETB.

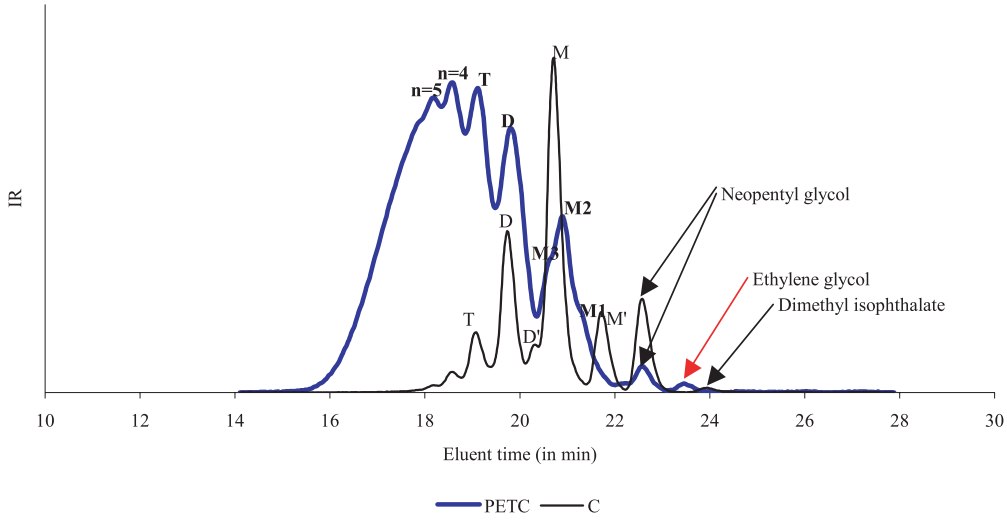


Fig. 3. SEC comparison of oligoester C and PETC.

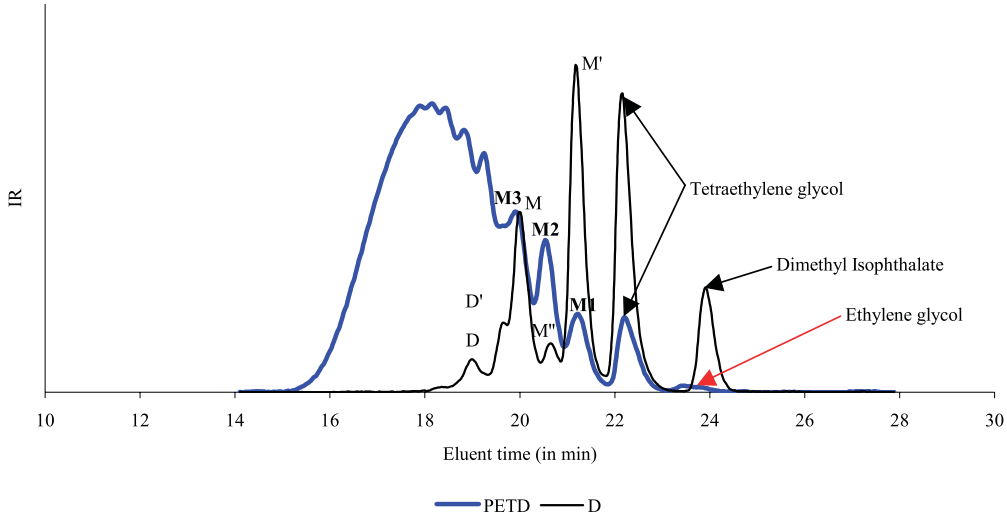


Fig. 4. SEC comparison of oligoester D and PETD.

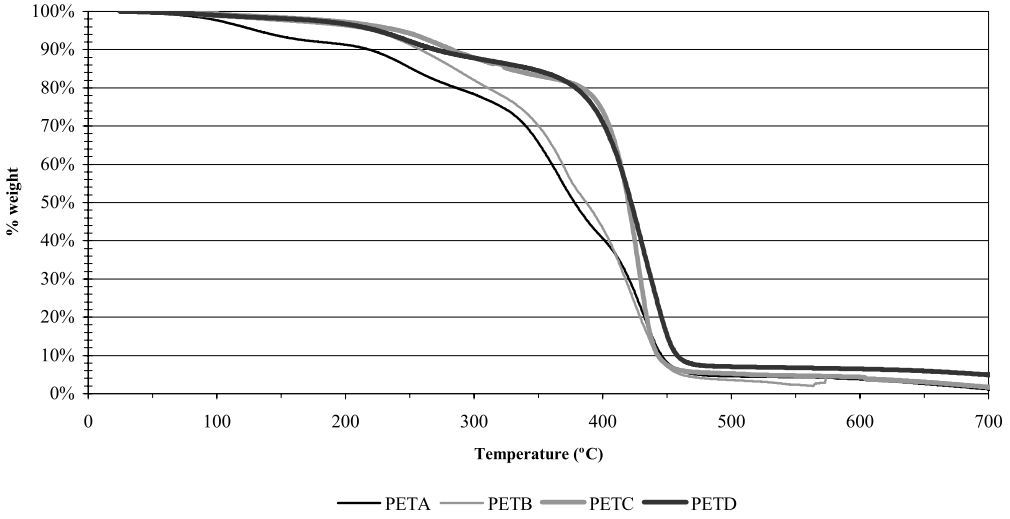


Fig. 5. TGA of the glycolysates.

different ways. The oligoesters introduce another ester segment in the glycolysate without ester formation kinetic problems. The diacids or dimethylesters react during the synthesis of the oligoesters. So it limits the formation of water or methanol during the glycolysis. These little molecules would increase the pressure in the reactor at high temperature.

The measures of the hydroxyl index and acid index of the glycolysates obtained are assembled in Table 3.

The acid values of the glycolysates were very low in respect to the hydroxyl indexes.

We can note that the acid function contents titrated after glycolysis are in the same range as those of the glycolysates or the oligoesters involved. However, the acid indexes are much higher for the oligoesters A and B, synthetised from a diacid way (uncompleted esterification reaction) than for oligoesters C and D, synthetised from a dimethylester way.The acid indexes vary in the order: A, B $\gg$ PETA, PETB, PETC, PETD $>$ C, D $\gg$ starting PET (Table 4). Thus, during the glycolysis time, carboxylic acids are concurrently consumed (probably by esterification reactions) and formed (probably either by ester thermolysis or by ester hydrolysis). Similarly, both NMR and Maldi-tof analyses, during the oligomers preparation, show uncompleted transesterification of dimethylesters, that continue almost to completion in the glycolysis step.

3.2. Characterizations

The products were characterized by FTIR, ^{1}H NMR, SEC and Maldi-tof. For these two last techniques, we observed an increasing complexity of the system from the oligoesters to the glycolysates. (Schemes 1–4).

In fact, the glycolysis of PET results in a succession of transesterification reactions being in equilibrium[11,12,32,35]. Thus, the real structure of the glycolysates corresponds to a mixture of α, ω diols. So, the glycolysate corresponds to a statistical copolymer containing all or part of four structural ester units and one end between two possible final diol groups (see Schemes 1–4).

We will see that this assumption is demonstrated by the characterization presented below.

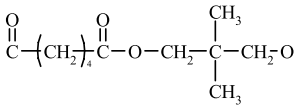
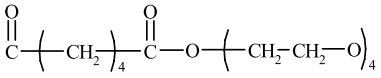
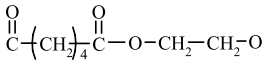
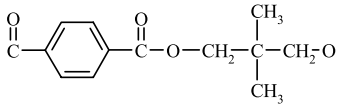
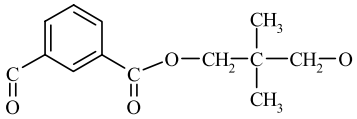
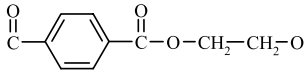
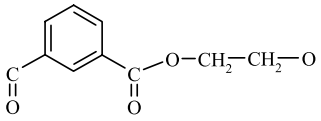
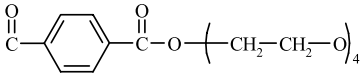
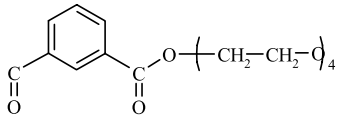
3.2.1. Steric exclusion chromatography (SEC) analysis

3.2.1.1. Oligoester A and PETA. The presence of ethylene glycol in the glycolysate was observed which shows that the PET was indeed glycolysated. From Table 2, it appears that

Table 5
Thermal properties of glycolysates measured by TGA and DSC

		PETA		PETB		PETC		PETD	
Thermogram analysis results	$T_{10\%}$ (°C)	219		258		283		270	
	$T_{20\%}$ (°C)	286		311		384		379	
	$T_{50\%}$ (°C)	378		387		420		422	
	$T_{90\%}$ (°C)	446		443		443		458	
DSC measurement		A	PETA	B	PETB	C	PETC	D	PETD
	T_g (°C)	−67	−34	−70	−52	−22	+6	−70	−28

Table 6
Possible segments in glycolysates

	Molecular formula	Molecular weight (g mol^{-1})
	$C_{11}H_{18}O$	214.3
	$C_{14}H_{24}O_7$	304.3
	$C_8H_{12}O_4$	172.2
	$C_{13}H_{14}O_4$	234.2
		
	$C_{10}H_8O_4$	192.2
		
	$C_{16}H_{20}O_7$	324.3
		

the molar ratio of acid end group is about 8% in oligoester A and <1% in PETA (Table 3); the adipic acid seems to be almost completely consumed during the reaction to form oligoester A (Fig. 1). Thus, two populations of polyesters may be expected for oligoester A (one series 'normal' with two hydroxyl end groups, and another one, called series, with one acid and one hydroxyl ends groups). Only the first population is expected for PETA, whereas populations with

Table 7
Oligomer population peaks of PETC (E=104.2) present in the MALDI-TOF spectrum

		m										
		0	1	2	3	4	5	6	7	8	9	10
n	0		361.1	595.2	829.4	1063.5	1297.6	1531.8	1765.7	2000.1	2236.5	2470.5
	1		553.2	787.3	1021.4	1255.5	1489.7	1723.9	1958.0	2193.2	2428.3	2660.0
	2	511.1	745.2	979.4	1213.5	1447.6	1681.8	1916.0	2152.1	2385.3	2620.3	
	3	703.3	937.3	1171.5	1405.6	1639.7	1874.9	2109.1	2343.2	2578.0		
	4	895.3	1129.4	1363.6	1597.5	1831.8	2067.0	2301.2	2536.2	2771.0		
	5		1321.4	1555.7	1789.6	2025.0	2259.1	2494.3	2728.3			
	6						2451.6					

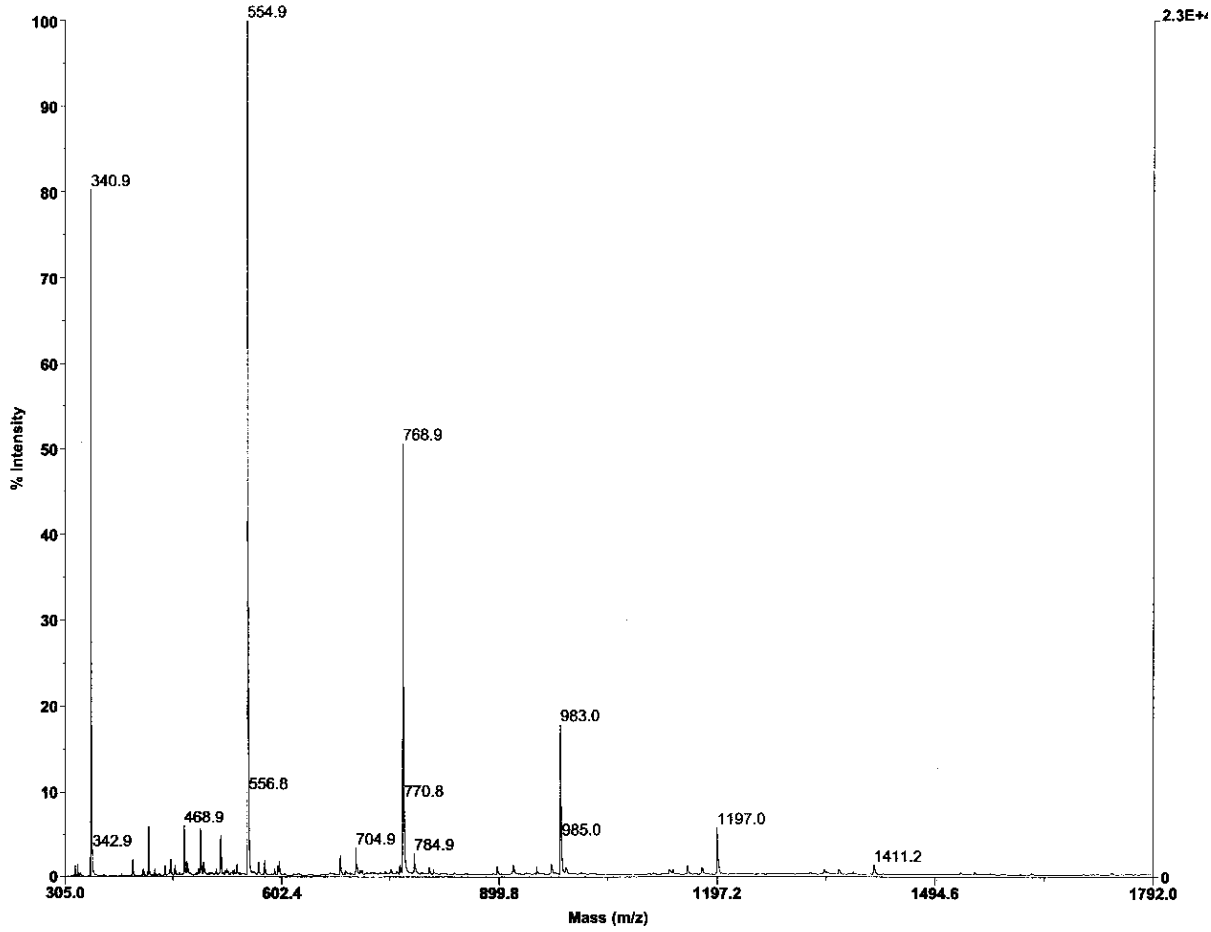


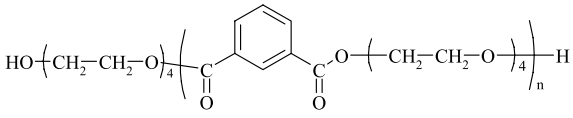
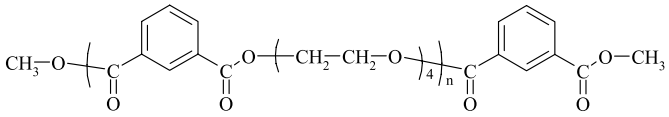
Fig. 6. MALDI-TOF spectrum of oligoester A.

two acid end groups appears mostly improbable (see Table 3, Fig. 7). Two supplementary products—monomer M′ and dimer D′—may be identified in the chromatogram of A (we call monomer, dimer, i-mer the products with one, two, i, diacid segments).

The hydrodynamic volumes of adipic and phthalic acid segments should be close. However, that of ethylene glycol would be noticeably smaller than that of neopentylglycol. Thus in PETA, according to [32], we can identify three peaks M1, M2 and M3 corresponding to monomers with two ethyleneglycol, one ethyleneglycol and one neopentylglycol, and two neopentylglycol, respectively. For dimer and higher oligomers, there are more possible products and the resolution of the SEC is insufficient to distinguish individual peaks. The Maldi-tof analysis could make it possible to refine the analysis of these peaks.

3.2.1.2. Oligoester B and PETB. We propose a similar interpretation of the chromatograms. However, the adipic acid seems not to be completely consumed during the

Table 8
Two possible different structures with the same molecular weight in oligoester D

	Possible structure present in oligoester D	Molecular mass of the compounds
Diol		$324.33n + 194.23$
Diester		$324.33n + 194.19$

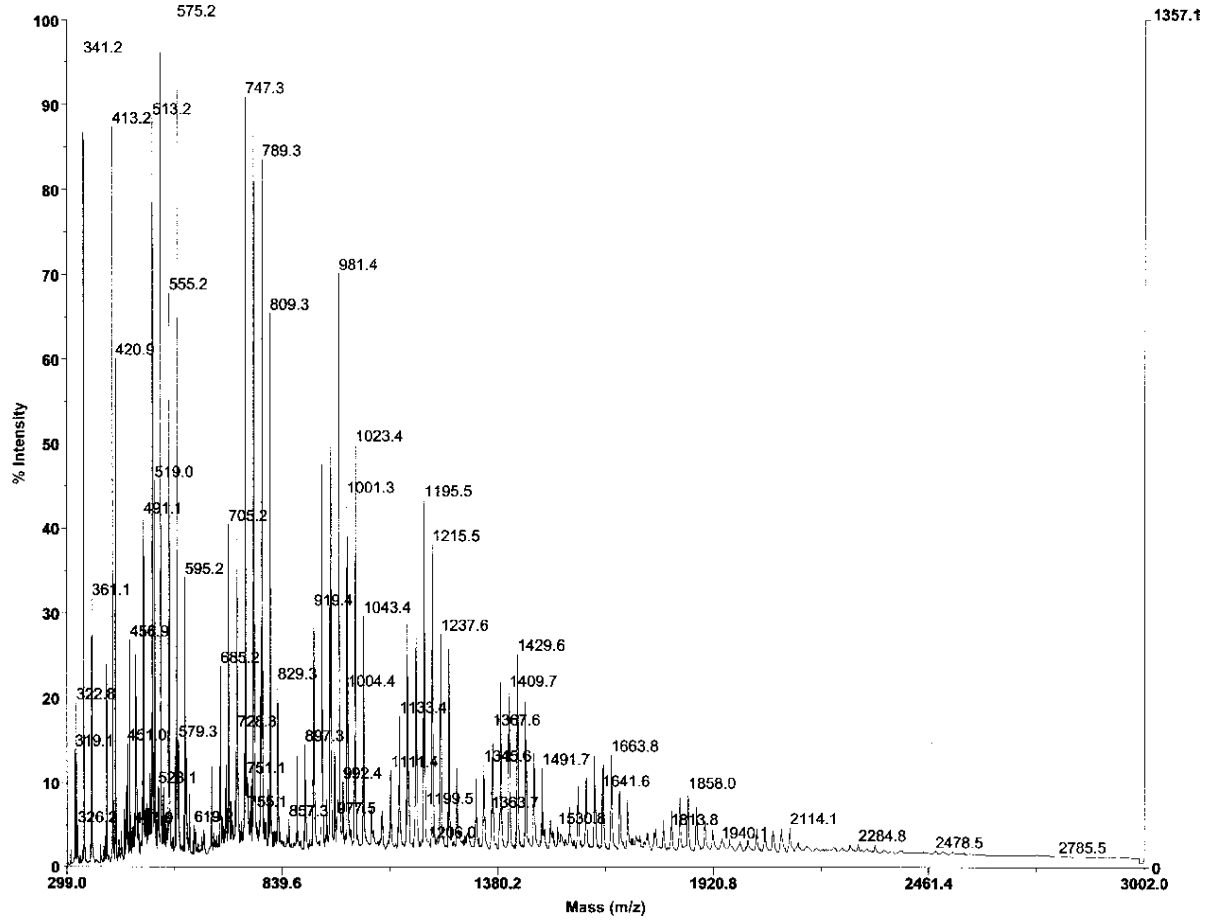


Fig. 7. MALDI-TOF spectrum of PETA.

reaction to form oligoester B (Fig. 2). The presence of ethylene glycol in the glycolysate was observed as previously, which shows that the PET was glycolysated. In the glycolysate PETB, residual adipic acid and tetraethylene glycol peaks seem to have diminished according to oligoester B spectrum. So we can estimate that these compounds were consumed during glycolysis.

Also, the molar volume of the tetraethyleneglycol segment is much higher than that of the others. Thus overlapping of (i-1)-mers (with TEG) and i-mers (without TEG) is probable. M1, M2 and M3 peaks could be identified in the monomer series of PET-B, but with overlapping of M3 and dimers.

3.2.1.3. Oligoester C and PETC. We propose a similar interpretation of the chromatograms. However, the diacid precursor is a dimethylester instead of a diacid. In Fig. 3, oligoester C spectrum shows the presence of a dimethyl isophthalate peak that disappears in PET-C. Thus, oligoester C should show one series (M′ and D′) with one neopentylglycol and one methyl isophtalate end groups. Considerable overlapping of peaks M1, M2 and M3 occurs. These peaks are absent in PETC spectrum which proves the consummation of these products during glycolysis. The presence of ethylene glycol in the glycolysate was noticed which shows that the PET was indeed glycolysated.

Table 9
Population peaks of alcohol-ended oligomers of PETD (E′ = 194.2) present in the MALDI-TOF spectrum

		m						
		0	1	2	3	4	5	6
n	0		541.2	865.3	1189.5	1513.6	1837.7	2161.8
	1	409.1	733.2	1057.4	1381.6	1705.8	2029.8	
	2	601.2	925.3	1249.5	1573.7	1897.9	2221.8	
	3	793.2	1117.3	1441.6	1765.8	2089.7		
	4		1309.5	1633.7	1957.6			
	5	1177.5	1501.6	1825.8	2149.7			

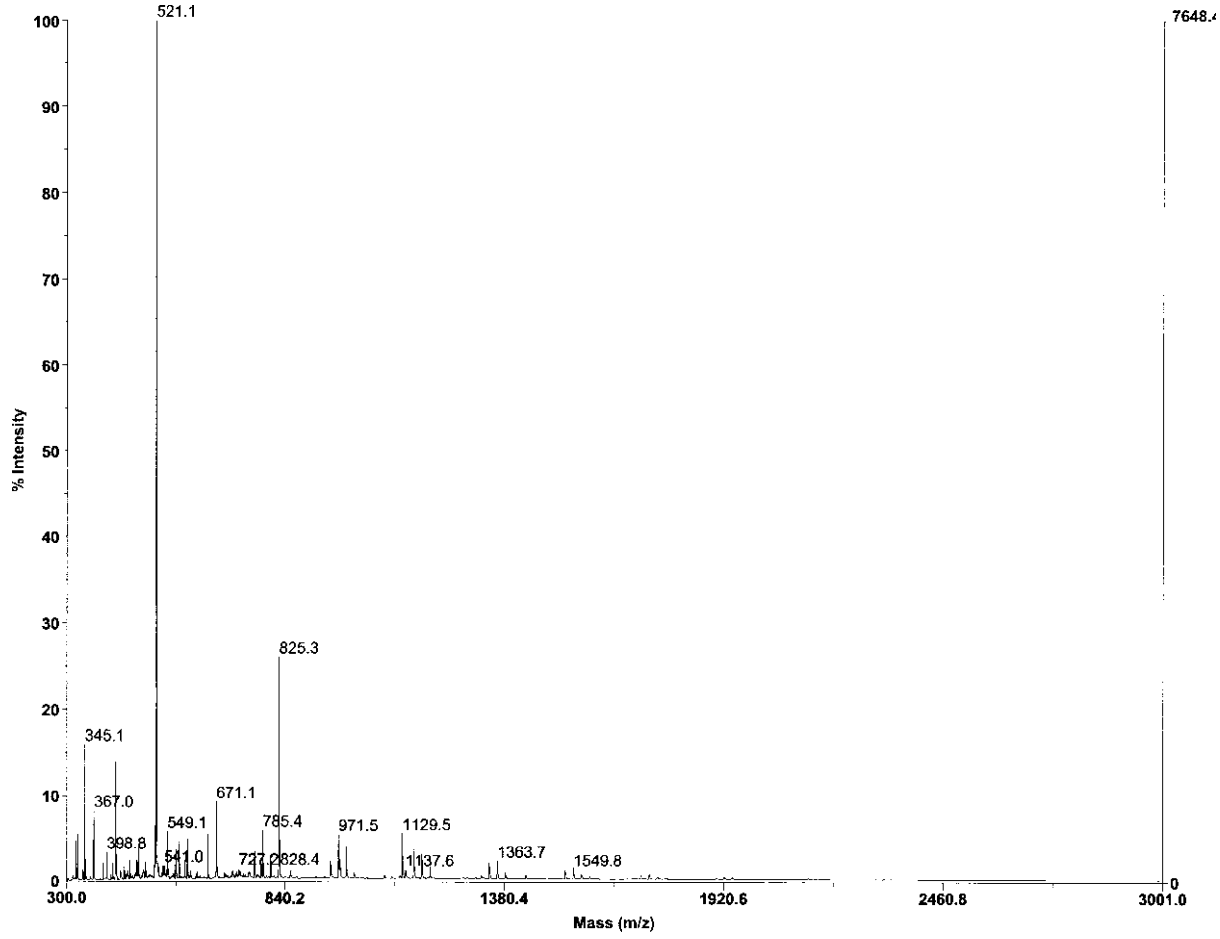


Fig. 8. MALDI-TOF spectrum of oligoester B.

3.2.1.4. Oligoester D and PETD. The SEC of D shows that the reaction between dimethyl isophthalate and TEG is not complete because a significant peak for residual dimethyl isophthalate is noticed (Fig. 4). However, that does not seem to be a disadvantage since the spectrum of the glycolysate shows the disappearance of this peak, indicating that residual methyl isophthalate is consumed during the glycolysis step. The yield of the transesterification of methyl esters is too low, so we can estimate the presence of 'one series' with two methoxy terminal groups and a supplementary M″ peak could be identified in D chromatogram. For PETD, considerable overlapping occurs between M3 and dimer peaks.

Except for PETD, we can notice that the residual acid or methyl ester functions which are present in the oligoesters react during the glycolysis step. The incomplete consummation of the diacid or dimethyl ester during the oligoester synthesis seems not to be a disadvantage for the glycolysis step.

3.2.2. Thermal properties

In our polyesters, the weakest links are the ester links: R-(O=)C–O– (ester thermolysis) and ether: R-C–O–C particularly in oxidative atmosphere. Moreover, aromatic esters are more stable than aliphatic ones, and NPG esters are stable due to the absence of proton substitution on the C in

Table 10
Population peaks of OCH_3 ended oligomers of PETD1 present in the MALDI-TOF spectrum

		m				
		1	2	3	4	5
n	0	379.1	703.2	1027.3	1351.6	1675.7
	1	571.1	895.3	1219.4	1543.6	1867.9
	2	763.1	1087.3	1411.6	1735.8	2060.0
	3		1279.5	1603.7		

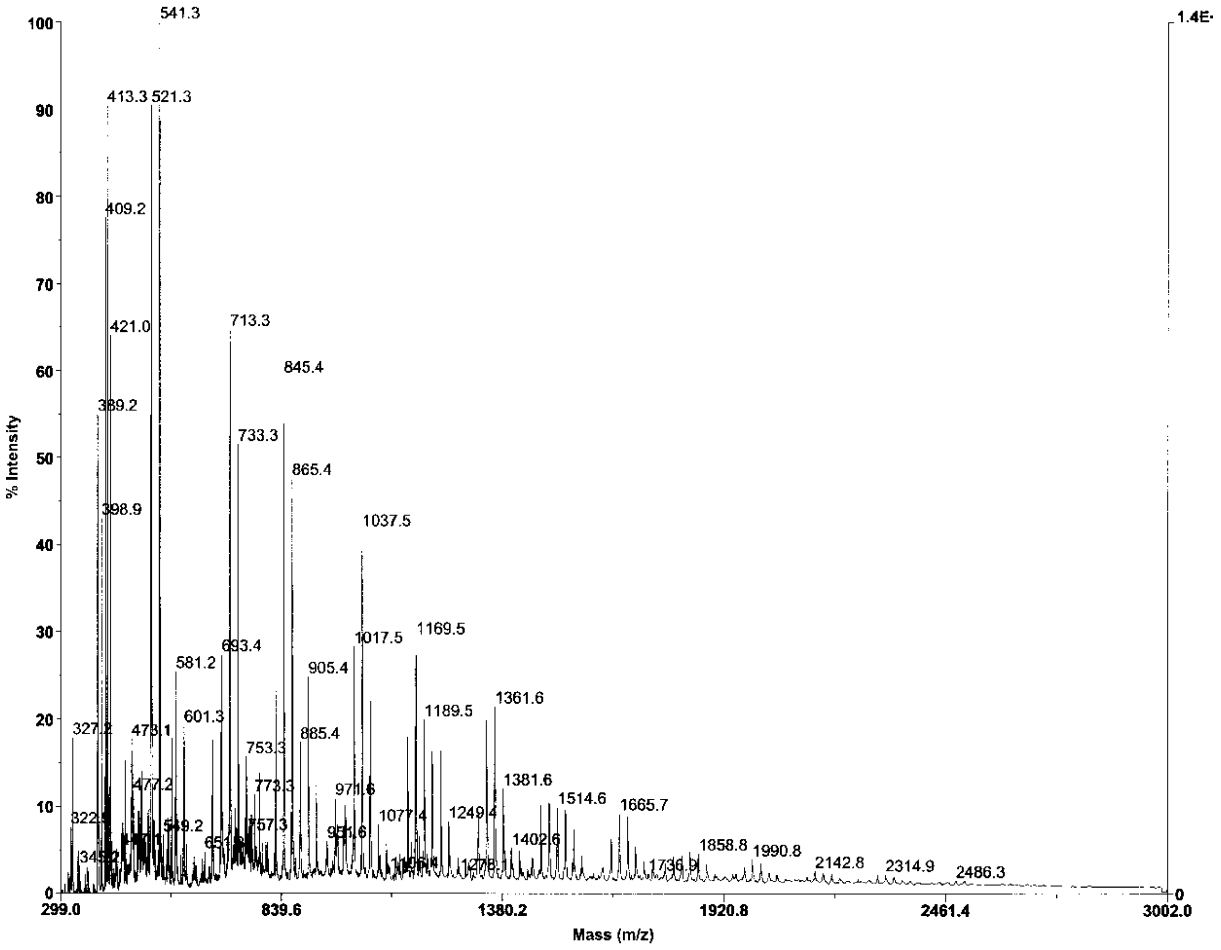


Fig. 9. MALDI-TOF spectrum of PETB.

β-position to the carbonyl group. The best thermal stability can be noticed for the glycolysates obtained with the oligoesters resulting from dimethyl isophthalate (Fig. 5). However, only slighty better stability of NPG copolymers is observed and only for isophthalate copolymers. The glycolysates being constituted of terephthalic ester segments, the resulting glycolysates obtained from PET and an aromatic diol have a better thermal stability (Table 5). Indeed, the glycolysis of the PET by an aromatic diol will give a glycolysate containing more aromatic segments than a glycolysate obtained starting from an aliphatic diol. However, the aromatic elements are well-known to bring thermal behavior to a material.

The T_g of all products was determinated by DSC (Table 5). According to the chemical structure of the glycolysate, T_g can vary between −52 °C and +6 °C. So, flexibility properties of TEG segment and adipic segment are clearly noticed as well as the rigidity properties of the phthalic segments.

Thus, we can see that the thermal properties of the polyesterdiols can be varied by adjusting their chemical composition.

3.2.3. MALDI-TOF analysis

In order to determine the structure of the different oligomers, it is necessary to determine the mass of the various constituent blocks in the oligomers. To simplify the problem, the glycolysates are a statistical succession of:

- repeating units of PET,
- repeating units of the oligoester,
- units constituted of terephthalic acid with the diol present in the previous oligoester.
- units constituted of the same diacid as in the oligoester with ethylene glycol.

In the same time, a hydroxyl chain end coming either from the diol of the oligoester or from ethylene glycol is presumed. The initial oligoesters were analyzed too.

Mori [36] and Dannoux [14] studied by MALDI-TOF the glycolysis of PET with one diol where two principal repeating units were noticed. In this paper, we studied the glycolysis by oligoesters with four different units. So, if we would sum up the results in a table, we should need a 4D table, which cannot be used in a paper. However, the possible blocks are those described in Table 6.

3.2.3.1. Oligoester A and PETA. In the spectrum of

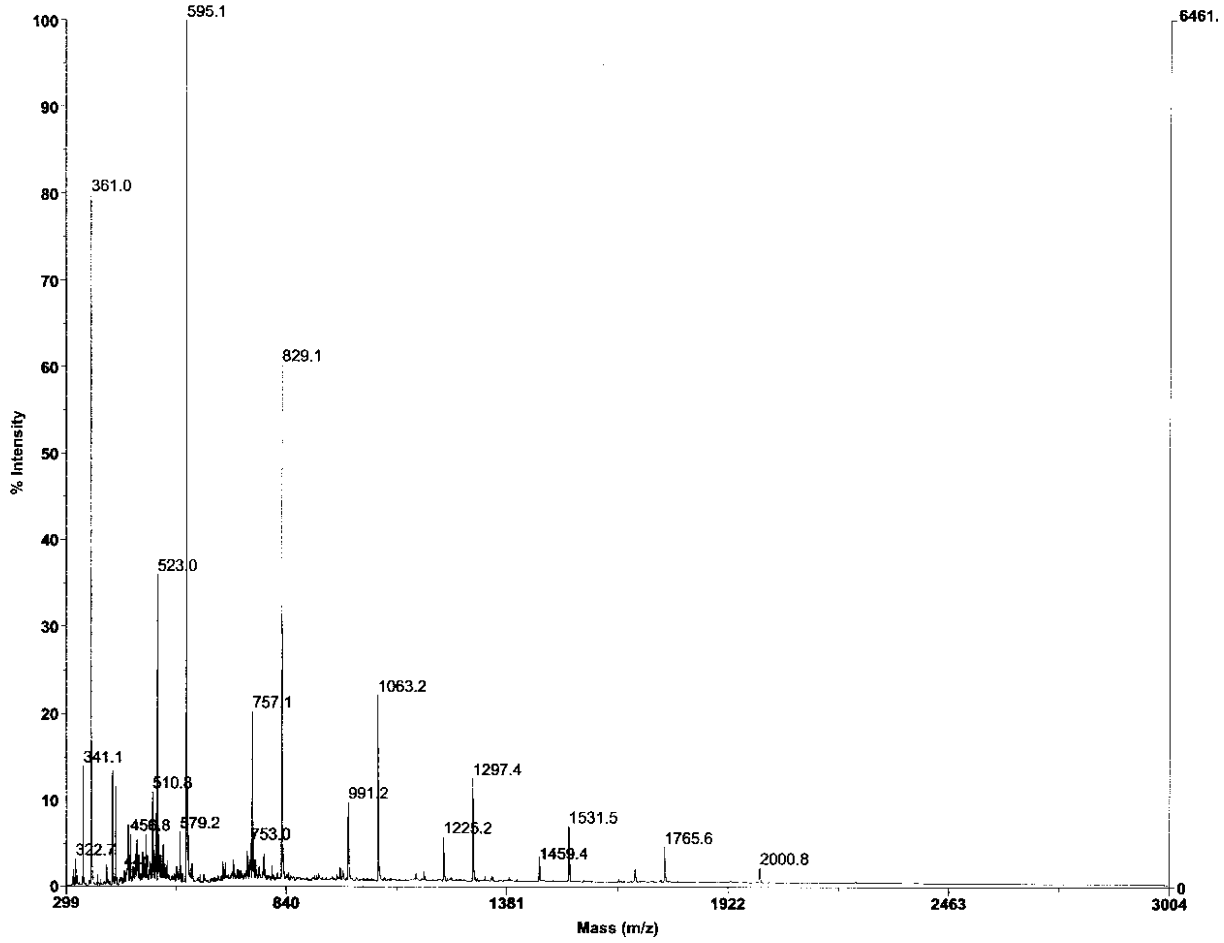


Fig. 10. MALDI-TOF spectrum of oligoester C.

oligoester A (Fig. 6), the main distribution appears from $m/z = 341$ Da, which represents MNa^+, where M is a diol and $l = 1$, to 1411 (DP from 1 to 6) (Scheme 1). The peaks are characterized by a mass increment of 214 Da from one peak to the next one which is the mass of repeating unit of the oligoester A made by adipic acid and neopentyl glycol. We noticed the presence of a peak at 469 Da which represents the compound $l = 1$ with one acid end and one hydroxyl end. Neither diacid, nor cyclic polyesters or di neopentyl segments compounds were noticed. All expected peaks were found. However, there are some unexpected significantly high peaks, that seem spaced from 28 Da from the compounds with one acid end and one hydroxyl end.

In the spectrum of PETA (Fig. 7), besides peaks below 315 Da that cannot be observed, the presence of all expected molecules is noticed for the monomers and dimers and trimers. (we can notice the very low intensity of peaks $n > 1$ with only ethylene glycol units, whose probability of existence in the equireactivity hypothesis is very low [32]). To sum up, PETA seems to have a maximum of eight monomeric ester units. This analysis proves the validity of multiple interchange reactions [32], leading to statistical copolymers. There are also some unexpected significantly high peaks, for example in the dimer region: 399, 413, 421, 519 Da. Different distributions with a mass increment of 192 Da (PET repeating unit mass) which correspond to the different combinations of the different repeating units as we can see in Scheme 1.

$$M = 192.2\mathbf{n} + 234.2\mathbf{m} + 214.3\mathbf{p} + 172.2\mathbf{q} + E + 23$$

$$E = 18.0 \text{ or } 104.2 \text{ or } 62.1$$

The main peaks were assigned but to sum up, PETA seems to have a maximum of eight units.

3.2.3.2. Oligoester B and PETB. In the spectrum of oligoester B (Fig. 8), the main distribution appears from $m/z = 521$ Da to 1433 (DP from 1 to 4), which represents MNa^+ and M is a diol and $l = 1$. The peaks are characterized by a mass increment of 304 Da from one peak to the next one which is the mass of the repeating unit of the oligoester B made by adipic acid and tetraethylene glycol. We noticed the presence of representative peaks of the compounds with one acid end and one hydroxyl end (345 Da: $l = 1$ and 649.68 Da: $l = 2$). No diacid compounds were noticed.

The spectrum of PETB (Fig. 9) leads to almost the same

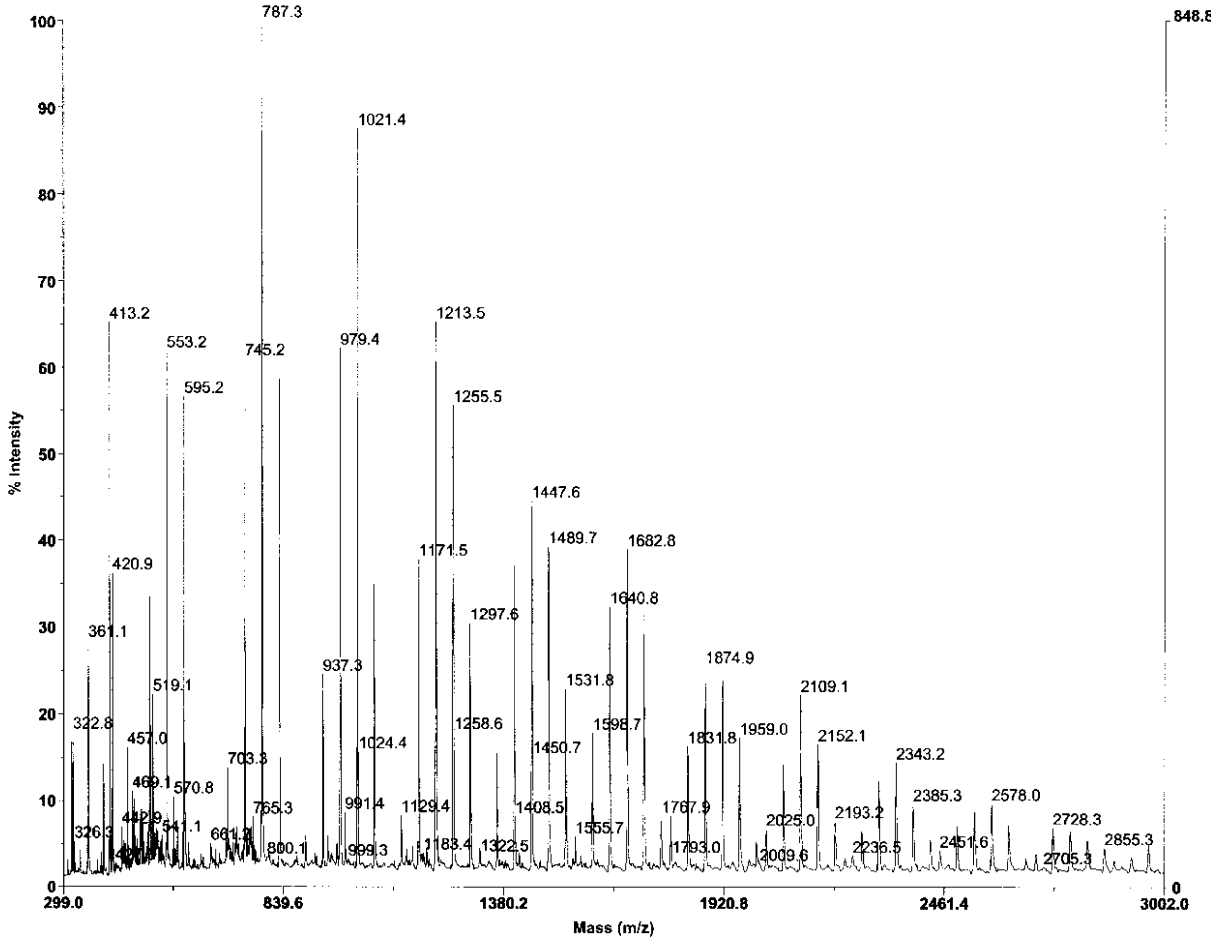


Fig. 11. MALDI-TOF spectrum of PETC.

conclusions as for PETA. There are also some unexpected significantly high peaks, for example in the dimer region: 413, 421, 473, 497, 671 and 785 Da. We noticed different distributions with a mass increment of 192 Da (PET repeating unit mass) which corresponds to the different combinations of the different repeating units as we can see in Scheme 2.

$$M = 192.2\mathbf{n} + 324.3\mathbf{m} + 304.3\mathbf{p} + 172.2\mathbf{q} + \mathbf{E}' + 23$$

$$\mathbf{E}' = 18.0 \text{ or } 194.2 \text{ or } 62.1$$

The majority of the peaks was assigned but to sum up, PETB seems to have a maximum of five units.

3.2.3.3. Oligoester C and PETC. In the spectrum of oligoester C (Fig. 10), the main distribution appears from $m/z = 361$ Da where M is a diol and $l = 1$, to 2001 (DP from 1 to 8) which represents MNa^+. The peaks are characterized by a mass increment of 234 Da from one peak to the next one which is the mass of repeating unit of the oligoester C issued from isophthalate and neopentyl glycol.

We noticed a second distribution with the same repeating units from $m/z = 523$ Da, $l = 2$ to 1459.4 (Dp from 2 to 6) which represents the compound with one ester chain end (CH_3O) and one hydroxyl chain end. No diester (OCH_3) chain end compounds were noticed.

It is noticed that the core isophthalate and terephthalate aromatic groups are isomers. The spectra of these glycolysates should thus consist in a more restricted number of populations.

The spectrum of PETC (Fig. 11), leads to almost the same conclusions as for PETA. It should be noted that the second distribution seen in the oligoester C did not give noticeable ions, that suggests that $COOCH_3$ functions did react during glycolysis. There are also some unexpected significantly high peaks, for example in the dimer region: 323, 413, 421, and 519 Da. We noticed different distributions from the main distribution of C with a mass increment of 192 Da (PET repeating unit mass) which corresponds to the different combinations of the different repeating units as we can see in Scheme 3 and Table 7

$$M = 192.04\mathbf{n} + 234.09\mathbf{m} + E + 23$$

with $\mathbf{n} = \mathbf{a} + \mathbf{b}$ and $\mathbf{m} = \mathbf{c} + \mathbf{d}$.

3.2.3.4. Oligoester D and PETD. In the spectrum of

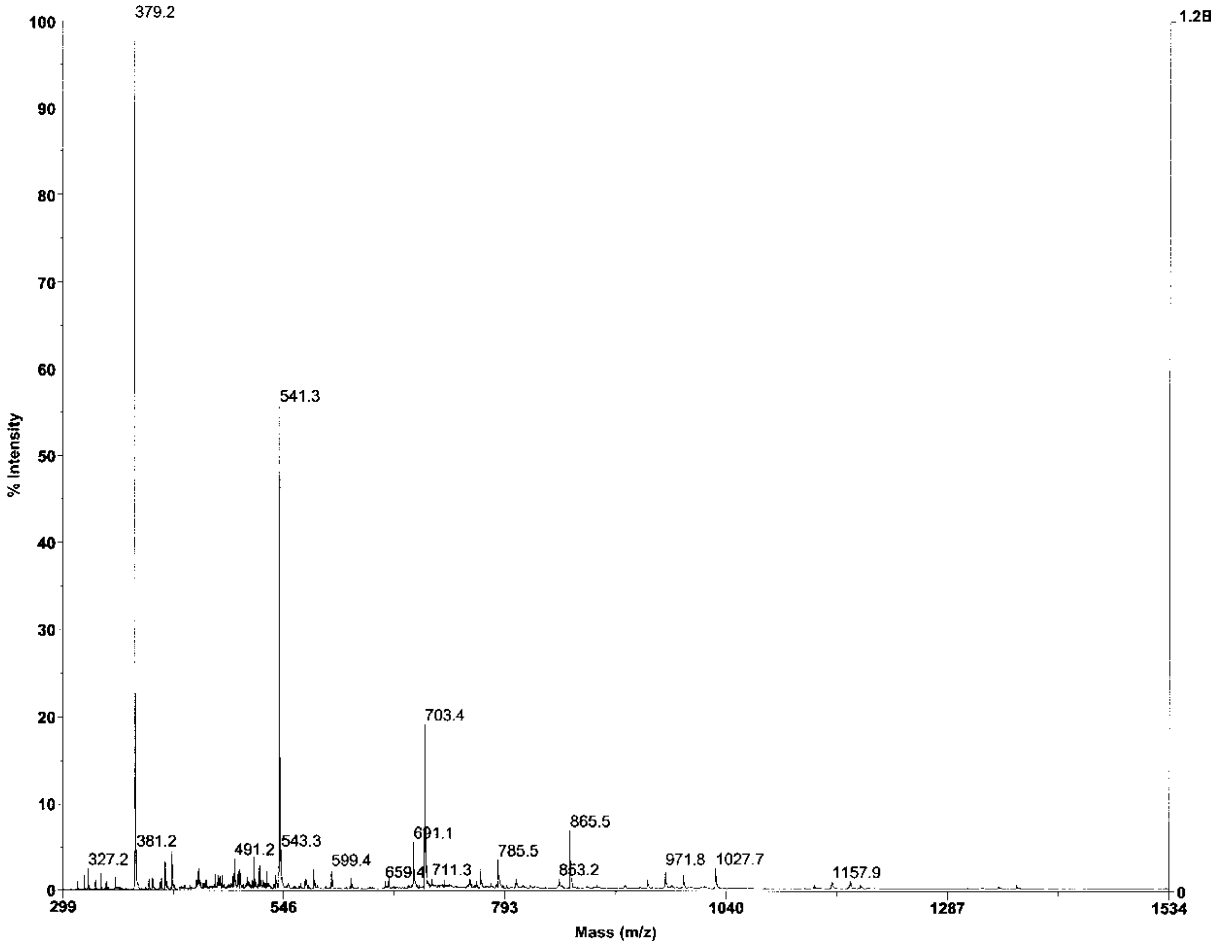


Fig. 12. MALDI-TOF spectrum of oligoester D.

oligoester D (Fig. 12), the main distribution appears from $m/z = 541$ Da which represents MNa^+ where M is a diol and $l = 1$ (Scheme 4), to 1189 (DP from 1 to 3). The spectrum of PETD (Fig. 11) leads to almost the same conclusions as for PETC. The peaks were characterized by a mass increment of 324 Da from one peak to the next one which is the mass of repeating unit of the oligoester D issued from isophthalate and tetraethylene glycol.

We noticed a second distribution with the same repeating unit from $m/z = 379$ Da, $l = 1$ to 1028 (Dp from 1 to 3) which represents the compound with one ester end (CH_3O) and one hydroxyl end.

(OCH_3) methylphthalate diester and the diol end compound having the same mass (Table 8), it is not possible to affirm the presence of two methoxy terminated esters. But according to the other compound, its presence is not very probable. There are also some unexpected significantly high peaks, for example in the dimer region.

In the spectrum of PETD (Fig. 13), we noticed different distributions from the main distribution of D with a mass increment of 192 Da (PET repeating unit mass) which corresponds to the different combinations of the different repeating units as we can see in Scheme 4 and Table 9.

$$M = 192.04\mathbf{n} + 324.12\mathbf{m} + E' + 23$$

with $\mathbf{n} = \mathbf{a} + \mathbf{b}$ and $\mathbf{m} = \mathbf{c} + \mathbf{d}$

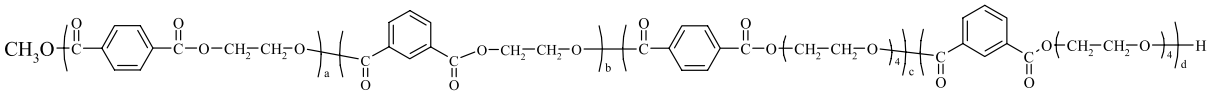
With a OCH_3 end (Table 10 and Scheme 5)

$$M = 192.04\mathbf{n} + 324.12\mathbf{m} + 32.03 + 23$$

with $\mathbf{m} = \mathbf{c} + \mathbf{d}$ and $\mathbf{n} = \mathbf{a} + \mathbf{b}$.

3.3. Properties and synthesis of the glycolysates

After cooling, the different glycolysates seem to remain



Scheme 5. Ester terminated glycolysate of PETD.

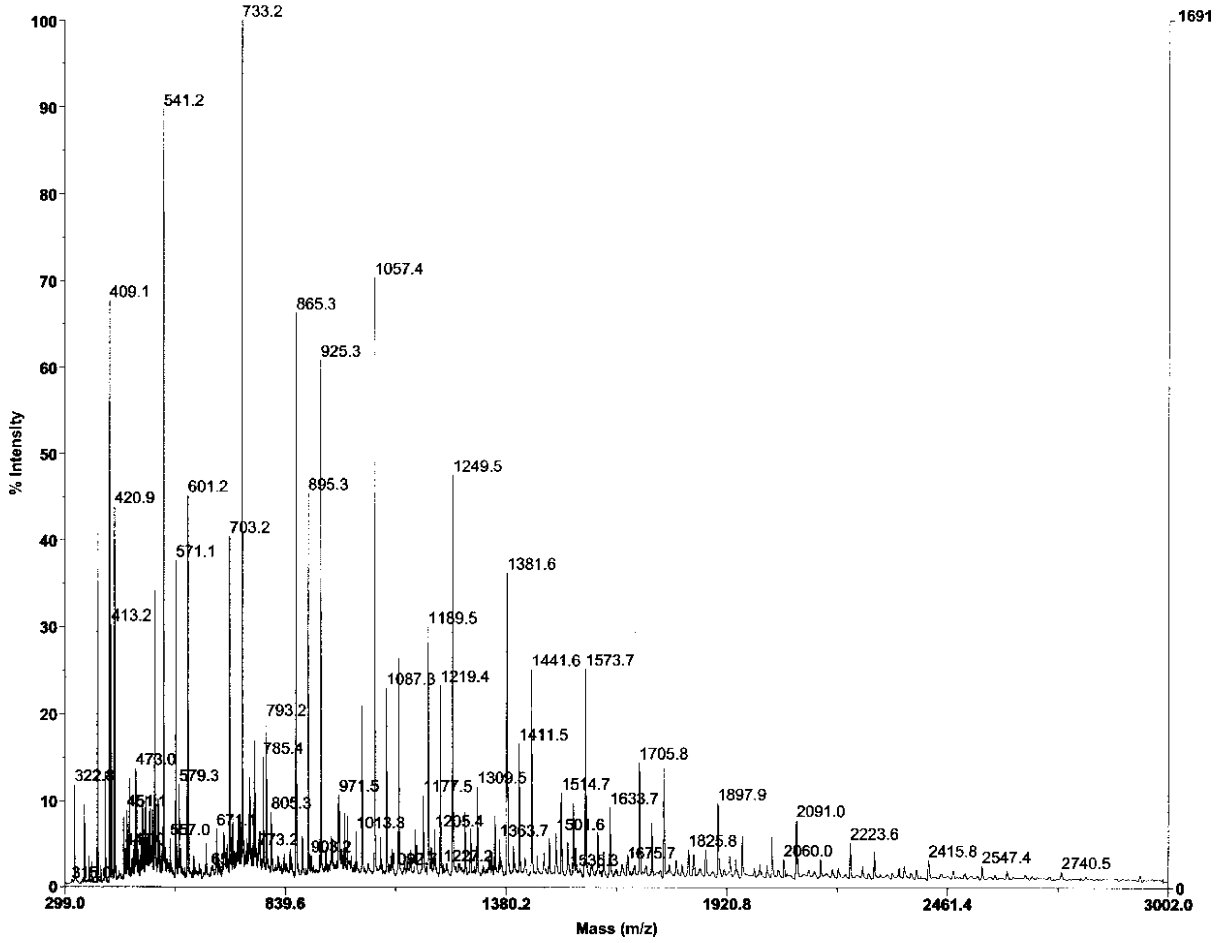


Fig. 13. MALDI-TOF spectrum of PETD.

as a homogeneous liquid during at least 6 months. However, the physical study of these products will be presented in another paper. The present work is focused on the chemical synthesis and characterization of these news glycolysates This work shows the influence of the oligoesters on the PET glycolysis process. In a preliminary study, we had used NPG or TEG alone in the glycolysis to reduce the crystallinity of the glycolysate and the results were convincing.

On one hand, TEG is a non crystalline long diol which reduces the crystallinity because of its flexibility. The same phenomenon occurs with DEG but TEG is longer. On the other hand, NPG is a short ramified diol, which reduces the crystallinity because of its ramified structure and its rigidity. At room temperature, the important viscosity of the glycolysate prevents the crystalline organization. The choice of the diacid was based on the same logic. Linear adipic segments give flexibility like TEG. Isophthalic segments which have not the same structure as terephthalic ones disturb the organization. Some isophthalic segments in a succession of terephthalic segments (PET) reduce the crystallization of the compound.

We can also notice that the reactivity of TEG is lower than that of NPG, what is exemplified by lesser esterification yields for identical process of oligoester synthesis (same temperature, time and molar amounts of diols and diacid derivatives). That could result from a dilution of the reactive functional groups, the molar volume of TEG being much higher. However, it is not necessary to conduct the oligoester synthesis to completion of esterification reactions. The remainder of the CO_2H or CO_2CH_3 groups are consumed during the high temperature glycolysis step within formation of only low amounts of volatile by-products. Thus, mild conditions (140 °C) may be adequate.

4. Conclusions

This study describes the synthesis of a new type of glycolysates using an oligoester type compound instead of a diol as described in numerous papers. The physical and thermal properties of the resulting glycolysates are linked to the nature of the diacid and diol segments involved in the oligoesters. All the analyses (NMR, SEC, Maldi-tof) confirm that the glycolysis step behaves as a succession of transesterification reactions being in equilibrium The MALDI-TOF analyses confirmed that the products coming from glycolysis are statistical copolymers made by a combination of PET units, of oligoester units and of

segments composed of esters of terephthalic acid with free diol resulting from the oligoester synthesis step.

The thermal analyses showed a dependence of both T_g and thermal stability of the glycolysates with the nature of the oligoesters. These glycolysates are potentially interesting in different areas as polyurethane formulation, thermoplastic elastomers, low V.O.C content.

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