Determination of oligomers in virgin and recycled polyethylene terephthalate (PET) samples by UPLC-MS-QTOF

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Abstract

An oligomer is a molecule that consists of a few monomer units. It can be formed during polymer manufacturing and also due to polymer degradation processes or even during use conditions. Since oligomers are not included in chemical databases, its identification is a complex process. In this work, the oligomers present in 20 different PET pellets samples have been determined. Two different sample treatment procedures, solvent extraction and total dissolution, were applied in order to select the most efficient one. The analyses were carried out by UPLC-MS-QTOF. The use of high resolution mass spectrometry allowed the structural elucidation of these compounds and its correct identification.

The main oligomers identified were cyclic as well as lineal from the first, second and third series. All of them were composed by terephthalic acid (TPA), diethylene glycol (DEG) and ethylene glycol (EG). Quantitative values were very different in both procedures. In total dissolution of PET samples, the concentration of oligomers was always, at least, 10 times higher than in solvent extraction, being some of the compounds only detected when total dissolution was used. Results showed that the oligomers with the highest concentration values were dimers and trimers, cyclic as well as lineal, from the first and second series. The oligomer with the maximum concentration value was TPA_2-EG-DEG, that was found in all the samples in a concentration range from 2493 to 19290 ng/g PET. No differences between virgin and recycled PET were found. Migration experiments were performed in 2 PET bottles, results showed the transference of most of these oligomers to a fat food simulant (ethanol 95%).

Keywords: non-intentionally added substances (NIAS); total dissolution; oligomers; polyethylene terephthalate (PET); food contact material; UPCL-MS-QTOF.

1. Introduction

Polyethylene terephthalate (PET) has been considered as one of the most important engineering polymers in the past two decades. It is regarded as an excellent material for many applications and is widely used for food packaging due to its physico-chemical properties such as good gas barrier properties, low diffusivity, good mechanical and thermomechanical properties, highly inert material, transparency and good processability (1-3). In addition, it can be said that probably is the polymer with the lowest number and concentration of additives, as the pristine properties make it appropriate for many applications, especially in food contact area. Another important advantage of PET as a packaging material is the good recyclability, low diffusivity and low uptake characteristics (4-9).

PET is manufactured by polymerization of ethylene glycol (EG) and terephthalic acid (TPA) or dimethyl terephthalate (DMT) during a polycondensation reaction. Amorphous preforms are obtained by processing the PET granules (pellets). Then, preforms are stretched by a blow-molding process to achieve bi-axially oriented bottles. Each step of this process could generate new substances that will be part of the polymer, posing a risk of unacceptable migration of these substances from PET bottles into foodstuffs in contact. They are defined as non-intentionally added substances (NIAS) and it is important to investigate their presence in each step of the manufacturing chain, in order to avoid its formation and therefore their presence in the final food contact materials (5, 8, 10-12).

The most common NIAS in PET polymers are oligomers. Their identification is difficult as they are not included in any database and there are not standards available. Thus, the identification of their chemical structure has to be done based on their fragmentation mass spectra and selecting different analysis conditions. Several oligomers have been identified in this work, either cyclic or open oligomers.

The main NIAS identified in this material were cyclic oligomers from the first and second series besides the lineal ones due to ring tension. The first series oligomers are composed by an equal number of terephthalic acid and ethylene glycol units, whereas in the second series, a single ethylene glycol unit is substituted by a diethylene glycol unit. Third series can also be formed, and in this case, two ethylene glycol units are replaced by two diethylene glycol units. The second and third series of oligomers arise because of the DEG formation during PET production as a by-product. All these oligomers have

potential to migrate into foods and for this reason their identification and quantification in PET used for food packaging is very important (13-19).

Since high concentration levels of the unknown compounds facilitate its identification, it is frequent to first analyse directly the polymer in order to identify the potential migrants. Fortunately, many of NIAS identified in the polymer will never migrate at a concentration level that could endanger the human health.

In this work, virgin and recycled PET pellets from different sources, were analysed by UPLC-MS-QTOF and the oligomers were identified and quantified to determine their oligomers profile. As sample treatment, two procedures were performed and compared: extraction with dichloromethane and total dissolution/precipitation, using hexafluoroisopropanol as solvent and methanol as antisolvent. The results are shown and discussed.

2. Material and methods

2.1 Reagents

A cyclic ester oligomer composed by diethylene glycol (DEG), adipic acid (AA) and isophtalic acid (IPA), AA-DEG-IPA-DEG (95% w), was used as standard for oligomers quantification. It was synthetized and provided by an adhesives company. Its structure and purity were confirmed by NMR. 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP, CAS 920-66-1) was purchased from Sigma-Aldrich Química S.A. (Madrid, Spain). Methanol and dichloromethane were purchased from Panreac (Barcelona, Spain). Methanol and water for UPLC analysis (ultra LC–MS quality) were obtained from Baker (Deventer, The Netherlands).

2.2 Samples

Twenty different samples of PET pellets were supplied by different manufacturing companies. Samples 01, 04, 07, 09, 15, 16 were virgin PET and samples 02, 03, 05, 06, 08, 10, 11, 12, 13, 14, 17, 18, 19, 20 were recycled PET. Two out of the 20 pellet samples were also available as bottles, PET15 and PET20. In order to reduce samples to powder, they were cryogenically cooled using liquid nitrogen and then ground using a knife mill under liquid nitrogen. In this way, there was an improvement in the extraction efficiency and a better sample homogeneity.

2.3 Sample preparation

Two different procedures were tested for sample preparation:

2.3.1 Total dissolution

An amount of 0.4 g of ground PET was weighed in a 20 mL glass vial and 4 mL of HFIP were added. The vial was closed with a screw cap and kept in an oven at 40ºC for 24 hours in order to assure the complete dissolution of the polymer. After this time, it was cooled down at room temperature and then, 8 mL of methanol were added as anti-solvent. The vial was shaken in order to guarantee a deep contact between solvent and polymer. Thus, the vial was kept at 4ºC for 1 hour to facilitate the polymer precipitation. The mixture was centrifuged at 4000 rpm for 10 minutes and the supernatant was extracted. Subsequently, the residual precipitated polymer was washed with 1 mL of pure methanol and the liquid phases were combined and weighed. Three replicates were prepared from each sample and several procedural blanks were also analysed.

2.3.2 Solvent extraction

An amount of 10 g of ground PET was weighed in a 100 mL glass container and three consecutive extractions with dichloromethane (DCM) were applied under the same conditions, but with different extraction volumes: 12 mL, 10 mL and 5 mL. In all of them the vial was kept in an ultrasonic bath for 1 hour and the supernatant was collected, filtered and transferred to a glass vial. The collected extracts were mixed together, evaporated to dryness under a gentle nitrogen current at low temperature and afterwards re-dissolved in 1 mL of methanol in ultrasonic bath. Finally, they were analyzed by UPLC-MS-QTOF. Three replicates and several procedural blanks were prepared from each sample.

2.4 Migration Test

Only 2 out of the 20 pellet samples were also available as bottles, PET15 and PET20. Migration test were performed with three food simulants for 10 days at 60ºC. Bottles were totally filled with simulant A (ethanol 10% v/v) and simulant B (acetic acid 3 % w/v) as aqueous simulants and ethanol 95 % v/v as fat simulant. Three replicates for each simulant were carried out. Simulants and test conditions used for the migration assays were chosen according to the European Regulation 10/2011 (20). The samples were analysed by UPLC-MS-QTOF. All the concentrations were corrected according to the

rate of 6 dm^2 of packaging material per 1 kg of simulant, in accordance with European Regulation 10/2011.

2.5 Instrumental analysis

2.5.1 Ultra-performance liquid chromatography (UPLC) coupled mass spectrometry detection with quadrupole-time-of-flight mass analyser (MS-QTOF)

The UPLC-MS-QTOF system consisted of an ACQUITY UPLC chromatograph coupled to a Xevo G2 QTOF mass spectrometer from Waters (Milford, MA, USA). An UPLC BEH C18 column (2.1 × 100 mm, 1.7 µm particle size) from Waters was used Flow rate was 0.3 mL/min, injection volume 10 µL and column temperature was set at 35 ºC. Mobile phase was water with 0.1% formic acid (A) and methanol with 0.1% formic acid (B). The separation was performed using a gradient elution: initial mobile phase A/B 98/2 was changed to A/B 0/100 over 6 minutes and afterwards maintained at this rate for 2 additional minutes.

Mass spectrometer was coupled to the UPLC system with an ESI probe. The following conditions were employed: positive ionization (ESI+) and negative ionization (ESI-), sensitivity mode, capillary voltage 2.5 kV, cone voltage 30 and 70 V, extraction cone 4 V, source temperature 120ºC, desolvation temperature 450 ºC, cone gas flow rate of 20 L/h, and desolvation gas flow rate of 700 L/h. Acquisition was performed in MS^E mode to allow using low and high collision energy (CE) in the collision cell during the same run. The mass spectrum at low energy (CE 4 V) provided information about the precursor ion (function 1) and the mass spectrum at high energy (CE ramp: from 15 to 30 V) information about fragment ions (function 2).

2.5.2 Identification of compounds detected by UPLC–MS-QTOF

A screening test of non-volatile compounds present in PET samples was carried out on the extracts obtained from total dissolution and solvent extraction. Three different acquisition conditions were used for the analysis; this allowed achieving an overall view of the potential oligomers. MassLynx (v. 4.0) software was used to acquire and process the chromatographic and MS data. With spectra from function 1, the elemental formula was obtained. Then, with the use of function 2, the fragmentation spectra were obtained and the proposed candidates were checked through MassFragment® software from Waters. This software enabled us to evaluate and confirm whether the product ions

detected in the high collision energy spectrum could be linked to the fragments generated from the chemical structures of the candidates proposed.

3. Results and discussion

PET oligomers were quantified by external calibration using the oligomer AA-DEG-IPA-DEG as standard. The working range in the instrument was 0.03-1.70 µg/g and the coefficient of determination (R^2) obtained in the calibration curve was 0.9994. The limit of detection (LOD) and quantification (LOQ) were 0.01 and 0.03 µg/g respectively. The LOD and LOQ were calculated as the minimum concentration whose signal was equal to 3 times and 9 times the baseline noise.

In total dissolution, the content of oligomers was calculated following equation 1:

$$[\text{Oligomer}]_{TD}\ (g / g_{PET}) = [\text{Oligomer}]_s \ x\ g_s / g_{PET} \qquad \textit{Equation 1}$$

where $[\text{Oligomer}]_s$ is the concentration in the supernatant (g/g) obtained from the interpolation in the calibration curve, g_s are the grams of supernatant after the polymer precipitation, and g_{PET} the grams of PET dissolved.

In solvent extraction, the content of oligomers was calculated according to equation 2:

$$[\text{Oligomer}]_{SE}\ (g / g_{PET}) = [\text{Oligomer}]_e \ x\ g_e / g_{PET} \qquad \textit{Equation 2}$$

where $[\text{Oligomer}]_e$ is the concentration in the methanol extract (g/g) obtained from the interpolation in the calibration curve, g_e are the grams of methanol used for the reconstitution of the extract and g_{PET} the grams of PET extracted.

3.1 Comparison between solvent extraction and total dissolution of PET samples

Four PET samples were analysed following the two different procedures described in section 2.3 to determine which procedure was more efficient to identify profile PET oligomers.

Table 1 summarizes the concentration of the four compounds detected in all the selected samples (PET 11, 12, 13, 14) and in both sample treatments, total dissolution and solvent extraction. All the compounds selected were oligomers coming from PET polymer. They were composed by terephthalic acid (TPA), diethylene glycol (DEG) and ethylene glycol

(EG): $(TPA\text{-}EG)_2$, TPA_2-EG-DEG, $(TPA\text{-}EG)_3$ and TPA_3-EG_2-DEG.

Some of the compounds, such as TPA_3-EG_2-DEG, were only detected when total dissolution was used. In total dissolution of PET samples, the concentration of oligomers was always, at least, 10 times higher than in solvent extraction. This was expected since in total dissolution, all the compounds will be present in the final extract, while in the solvent extraction procedure; the presence of compounds is limited by the surface of PET particles in contact with the solvent, the partition coefficient between PET and the solvent used for extraction and the physico-chemical properties of the compounds. The conditions applied for total dissolution were quite mild, so, the compounds identified cannot be attributed to the degradation of the polymer, as usually happens at high temperature. Therefore, total dissolution is recommended as sample treatment to know the potential migrants of the polymer.

3.2 Identification of oligomers in PET samples by UPLC-MS-QTOF and analytical features

Twenty PET pellet samples were analysed using the total dissolution protocol described in section 2.3.1. Table 2 shows the 14 PET oligomers identified and quantified by UPLC-MS-QTOF (21) and their concentration range in those samples where they were detected above the limit of detection (LOD). Relative standard deviation was always below 20%. Ten cyclic and 4 lineal oligomers were detected, all of them composed by terephthalic acid (TPA) and ethylene glycol (EG) or diethylene glycol (DEG). Dimers, trimers, tetramers as well as pentamers were observed. Lineal structures were only detected for dimers and trimers.

This analysis revealed three series of oligomers. In the first one, made up with oligomers containing only EG and TPA *(TPA_nEG_n),* seven different oligomers were determined, both cyclic and lineal: TPA-EG, $(TPA\text{-}EG)_2$+H_2O, $(TPA\text{-}EG)_2$, $(TPA\text{-}EG)_3$+H_20, $(TPA\text{-}EG)_3$, $(TPA\text{-}EG)_4$ and $(TPA\text{-}EG)_5$. In the second series, where one EG monomer is replaced by a DEG unit *(TPA_nEG_{n-1})DEG*, five oligomers were identified: TPA_2-EG-DEG+H_2O, TPA_2-EG-DEG, TPA_3-EG_2-DEG+H_2O, TPA_3-EG_2-DEG and TPA_4-EG_3-DEG. Finally, in the third series, where two EG monomers are replaced by two DEG units *(TPA_nEG_{n-2})DEG_2,* only 2 cyclic oligomers were detected, $(TPA\text{-}DEG)_2$ and TPA_4-EG_2-DEG_2.

The frequency of occurrence of all oligomers was compiled and is shown in table 2. The absolute frequency of occurrence for each oligomer is based on recording the number of

PET samples that contains that oligomer. The relative frequency of occurrence of each oligomer is related to the total number of samples analysed and expressed as percentage. The cyclic dimer of second and third series, TPA_2-EG-DEG and $(TPA\text{-}DEG)_2$; cyclic trimer of first and second series, $(TPA\text{-}EG)_3$ and $TPA_3\text{-}EG_2\text{-}DEG$; and cyclic tetramer of first series, $(TPA\text{-}EG)_4$, were identified in all samples so the relative and absolute frequencies of occurrence were 100%. The oligomer with the maximum concentration value was TPA_2-EG-DEG, that was found in all the samples in a concentration range from 2493 to 19290 ng/g PET. All PET oligomers have common fragmentation spectra which confirm the similarity of their structures (18). Their common masses are 149.0240, 193.0503, 341.0659 and 385.0918 m/z. Fig 1a shows the high collision energy spectra of a second series PET dimer, lineal (up) and cyclic (down). Fig 1b shows high collision energy spectra of first series PET dimer, lineal (up) and cyclic (down). Fragments observed successfully matched with the proposed structures.

As expected according to previous literature, the main compounds identified in PET samples were the cyclic and lineal dimers and trimers from the first and second series, (13, 14, 17, 22, 23), being the dimers from the second series the most abundant ones. The cyclic dimer from the third series was also found at relative high concentration. It can be also highlighted that cyclic oligomers were much more abundant than the lineal ones (Fig. 2). Furthermore, fig 3a shows the concentration of the 5 oligomers with the highest concentration in the 20 PET samples in order to see its distribution. The oligomers distribution was different in the studied samples. No visual differences in the concentration of the main oligomers was observed between virgin (V) and recycled (R) PET samples. A principal component analysis was also carried out with Unscrambler X software (Camo S. A) in order to check if there was a statistical sample grouping taking into account all the oligomers present in the samples. PCA results did not show any aggrupation between virgin and recycled samples. A Pearson correlation analysis was also performed with the normalized concentration values. Normalized values of each variable were calculated by subtracting the average and dividing by the standard deviation. High correlation values were found between TPA_2-EG-DEG and $TPA_3\text{-}EG_2$-DEG (0.8639) TPA_2-EG-DEG and $TPA_3\text{-}EG_2$-DEG (0.9186), cyclic and lineal respectively, dimer and trimer of the second series. Fig 3b and 3c show the profiles of these compounds in the different samples.

Fig 4 shows four chromatograms of dimers (*a-d*) and four chromatograms of trimers (*e-h*). Chromatograms *a, b, e,* and *f* show lineal and cyclic second series respectively,

figures *c, d, g*, and *h* show lineal and cyclic first series respectively. Fig 4 also shows that those oligomers that contain more DEG units (2 and 3 series) eluted on the leading edge of all EG oligomers. Furthermore, lineal oligomers eluted firstly than the corresponding cyclic ones (15).

Other non-volatile compounds likely present in the PET samples have not been presented in this work.

3.3 Content of oligomers in migration

Table 3 shows the concentrations of the oligomers identified in migration test. None of the oligomers was found in aqueous food simulants, ethanol 10% or acetic acid 3%. Seven oligomers were identified and quantified in migration to ethanol 95%, 5 of them (TPA_2-EG-DEG, $(TPA\text{-}DEG)_2$, $(TPA\text{-}EG)_3$, TPA_3-EG_2-DEG and $(TPA\text{-}EG)_4$) were previously detected in pellet samples with the highest concentrations. Among the oligomers detected, TPA_2-EG-DEG was the most abundant in the migration solution. Since these compounds are not present in EU/10/2011, their concentration should be below 10 ng/g (20). Most of these oligomers had been previously detected in migration by other authors (17, 18).

4. Conclusions

Total dissolution using hexafluoroisopropanol/methanol as solvent/antisolvent system, is recommended as sample treatment in order to identify and quantify the potential migrants of PET samples. Liquid extraction from PET provided incomplete qualitative information about oligomers, and very different quantitative values. A total of 20 samples, virgin and recycled, have been analysed and the oligomers present have been identified and quantified. Results provided a complete overview of the oligomers that can be found in PET pellets and the range of concentration. This information would allow evaluating the suitability of PET pellets for the manufacturing of food contact materials. Fourteen oligomers composed by terephthalic acid, ethylene glycol and diethylene glycol were detected, both cyclic and lineal, and their chemical structure was elucidated. Among them, 6 were of the first series, 5 of second series and 2 of third series. The oligomers detected with the highest concentration in the studied samples were the cyclic and lineal dimers and trimers from the first and second series. UPLC-MS-QTOF is very useful for the determination of oligomers content in PET samples as well as the presence of non-volatile additives and other NIAS. The identified oligomers have shown to be able to

migrate to food simulants in the studied samples, and this fact confirms the importance of knowing the oligomers composition in the raw material. This would allow evaluating its suitability for manufacturing the food contact materials.

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6. Compliance with ethical standards

The authors declare that they do not have potential conflicts of interest. No human participants or animals are involved in the research

7. References

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Table 1 Quantification of non-volatile compounds identified in PET11, PET12, PET13, PET14 samples in total dissolution (TD) and solvent extraction (SE). Retention time (rt), measured mass (mass), compound candidate and molecular formula (MF).

No	rt mass	Candidate MF	**PET11 (ng/g PET)**		**PET12 (ng/g PET)**		**PET13 (ng/g PET)**		**PET14 (ng/g PET)**	
			TD	SE	TD	SE	TD	SE	TD	SE
1	7.51 451.1001	TPA_2-EG-DEG $C_{22}H_{20}O_9$	16400±43	949 ± 46	13800±886	1280±22	16000±1100	1257±40	13100±794	1158±13
2	8.10 407.0730	$(TPA\text{-}EG)_2$ $C_{20}H_{16}O_8$	996±11	60 ± 4	873±35	79±11	770±91	76±1	<LOQ	<LOD
3	8.45_8.64 599.1180	$(TPA\text{-}EG)_3$ $C_{30}H_{24}O_{12}$	4810±106	73 ± 8	4510±232	102±12	5424±42	<LOD	5390±619	<LOD
4	8.49 643.1443	TPA_3-EG_2-DEG $C_{32}H_{28}O_{13}$	1880±4	<LOD	1590±169	<LOD	1741±45	<LOD	1950±249	<LOD

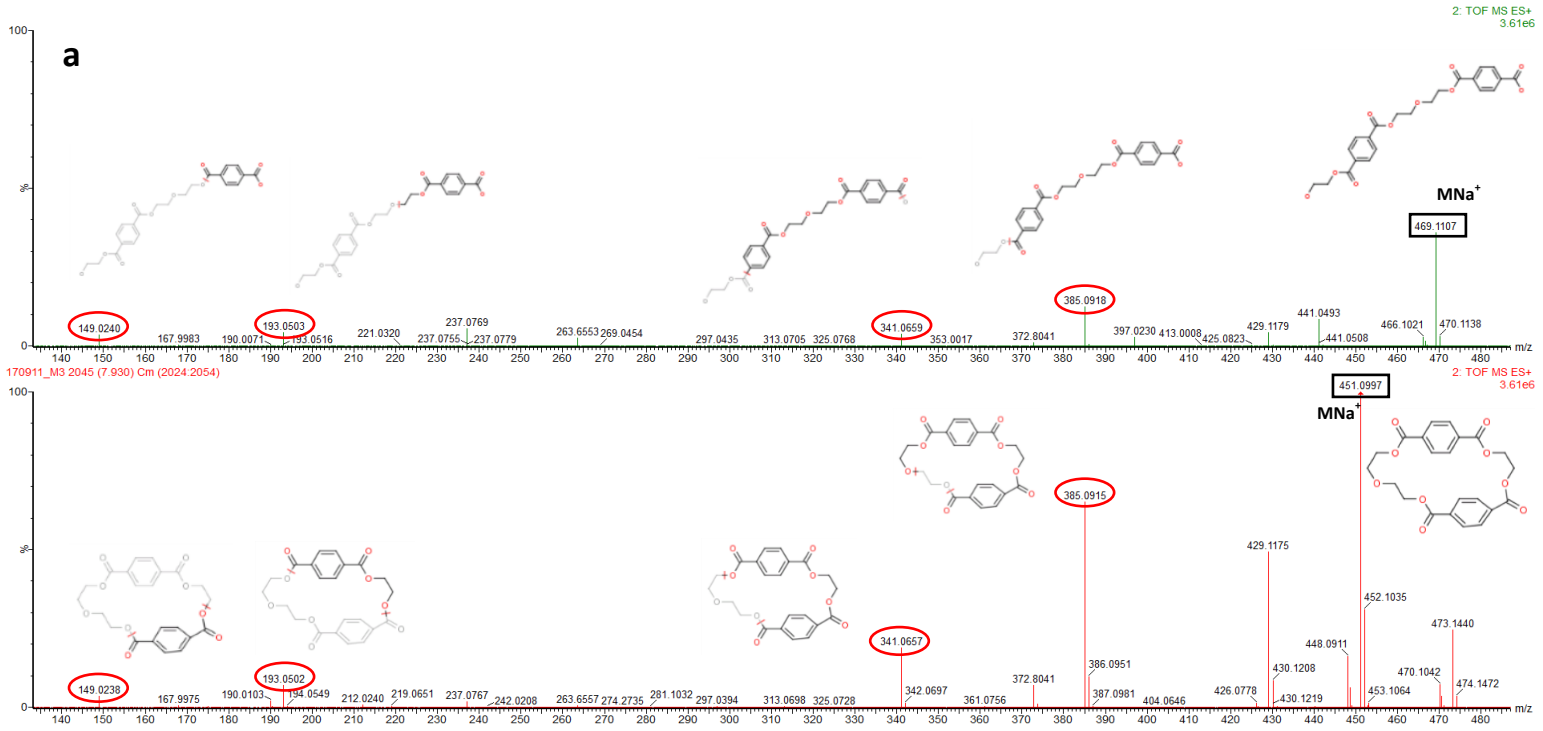
TPA: terephthalic acid; DEG: diethylene glycol; EG: ethylene glycol; LOD: limit of detection

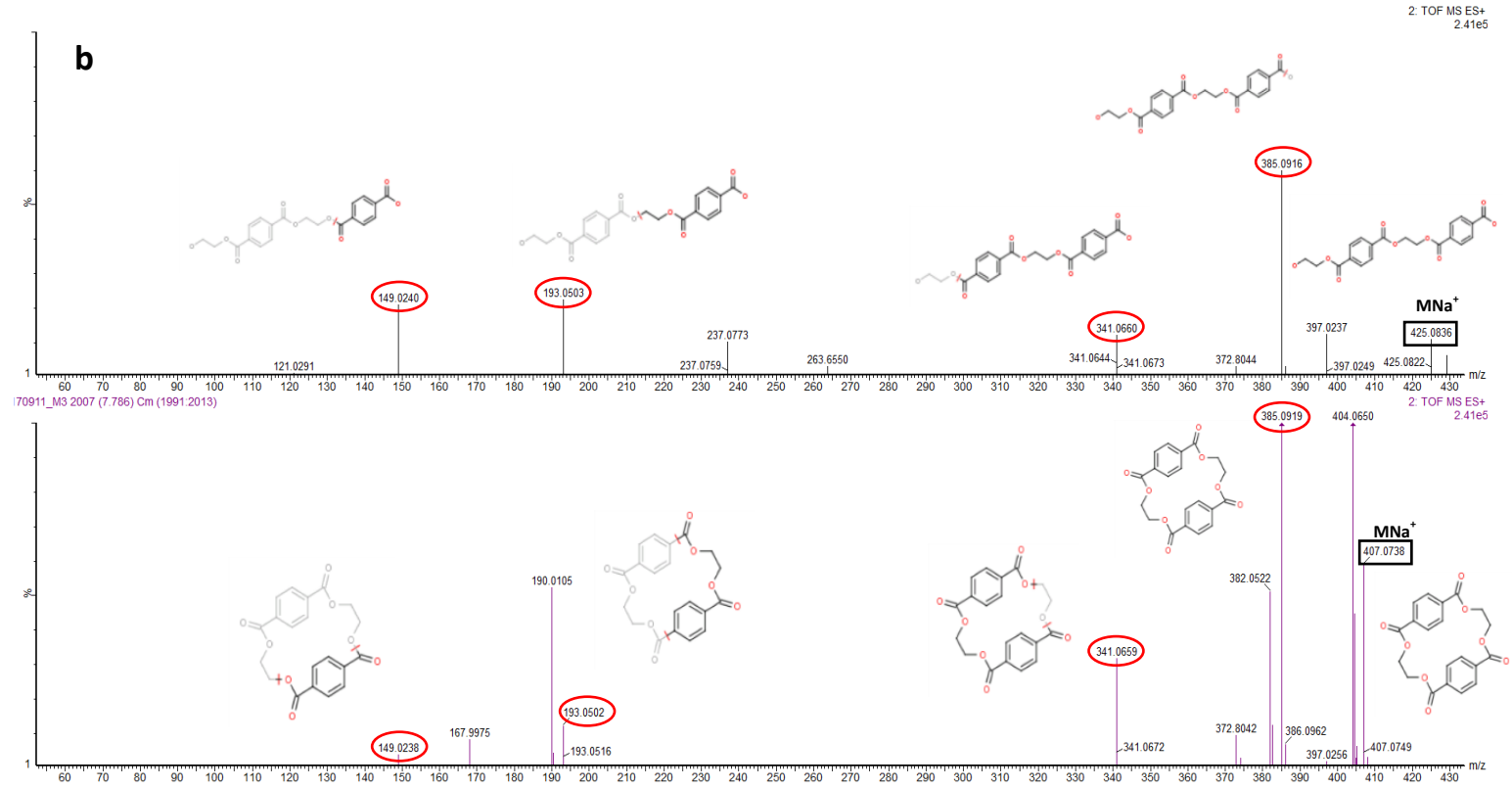
Table 2 Oligomers identified in total dissolution in 20 samples of PET pellets. Retention time (rt), measured mass (mass), type of ion found (adduct), compound candidate, molecular formula (MF), range of concentration and occurrence of oligomers in PET pellets.

No	rt	mass	Adduct	Candidate MF	Remarks	Concentration (ng/g PET)	Absolute Frecuency of Occurrence	Relative Frecuency of Occurrence (%)
1	6.79	469.1104	$[MNa]^+$	TPA_2-EG-DEG+H_20 $C_{22}H_{22}O_{10}$	Lineal dimer 2 series	183-7719	14	70
2	6.84	193.0498	[MH]+	TPA-EG $C_{10}H_8O_4$	Cyclic monomer	183-270	14	70
3	6.85	425.0843	$[MNa]^+$	$(TPA\text{-}EG)_2$+H_2O $C_{20}H_{18}O_9$	Lineal dimer 1series	183-507	18	90
4	7.32	495.126	$[MNa]^+$	$(TPA\text{-}DEG)_2$ $C_{24}H_{24}O_{10}$	Cyclic dimer 3 series	685-4843	20	100
5	7.35	451.0999	$[MNa]^+$	TPA_2-EG-DEG $C_{22}H_{20}O_9$	Cyclic dimer 2 series	2493-19290	20	100
6	7.35	879.21	$[MNa]^+$	TPA_4-EG_2-DEG_2 $C_{44}H_{40}O_{18}$	Cyclic tetramer 3 series	183-1102	19	95
7	7.54	661.1524	$[MNa]^+$	TPA_3-EG_2-DEG+H_20 $C_{32}H_{30}O_{14}$	Lineal trimer 2 series	183-1370	14	70
8	7.63	617.1263	$[MNa]^+$	$(TPA\text{-}EG)_3$+H_20 $C_{30}H_{26}O_{13}$	Lineal trimer 1 series	183-697	14	70
9	7.79	407.0738	$[MNa]^+$	$(TPA\text{-}EG)_2$ $C_{20}H_{16}O_8$	Cyclic dimer 1 series	183-1248	18	90
10	8.18	643.1419	$[MNa]^+$	TPA_3-EG_2-DEG $C_{32}H_{28}O_{13}$	Cyclic trimer 2 series	335-2219	20	100
11	8.3	599.1158	$[MNa]^+$	$(TPA\text{-}EG)_3$ $C_{30}H_{24}O_{12}$	Cyclic trimer 1 series	661-6978	20	100
12	8.5	835.1839	$[MNa]^+$	TPA_4-EG_3-DEG $C_{42}H_{36}O_{17}$	Cyclic tetramer 2 series	183-591	14	70
13	8.84	791.1578	$[MNa]^+$	$(TPA\text{-}EG)_4$ $C_{40}H_{32}O_{16}$	Cyclic tetramer 1 series	610-848	20	100
14	8.95	983.1998	$[MNa]^+$	$(TPA\text{-}EG)_5$ $C_{50}H_{40}O_{20}$	Cyclic pentamer 1 series	183-169	10	50

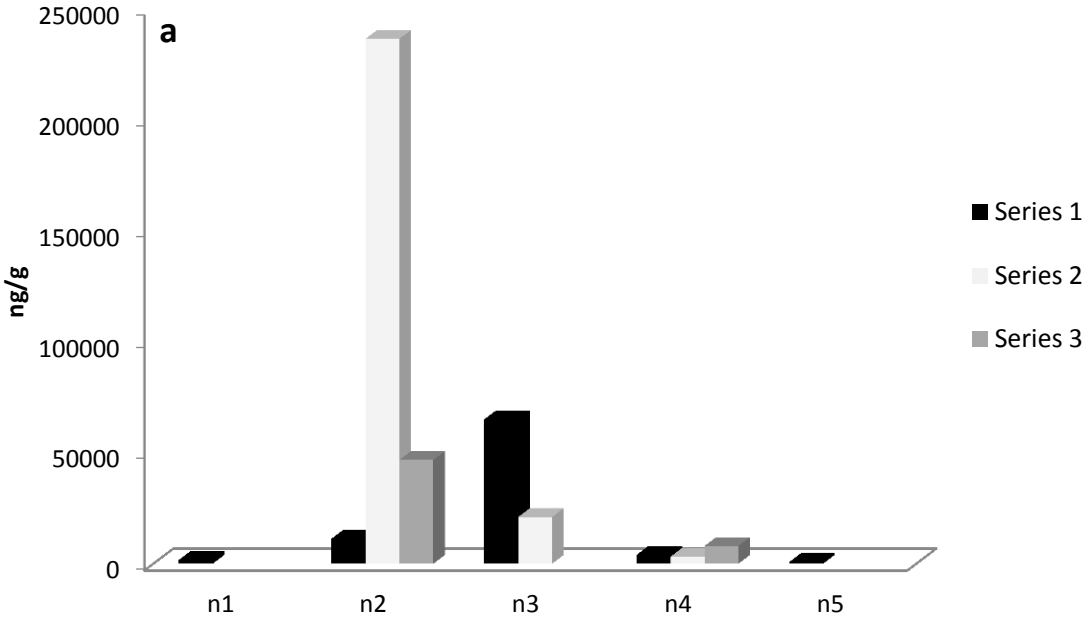
Table 3. Concentration of oligomers (ng/g) in migration from PET bottles to ethanol 95%.

Samples	$(TPA\text{-}EG)_2$	$TPA_2\text{-}EG\text{-}DEG$	$(TPA\text{-}DEG)_2$	$(TPA\text{-}EG)_3$	$TPA_3\text{-}EG_2\text{-}DEG$	$TPA_3\text{-}EG_2\text{-}DEG + H_20$	$(TPA\text{-}EG)_4$
PET15	24.41 ± 9.00	275.87 ± 7.91	60.39 ± 11.63	189.65 ± 3.67	43.08 ± 2.68	43.04 ± 4.48	<LOQ
PET20	<LOD	21.27 ± 1.35	<LOD	30.58 ± 1.31	<LOQ	<LOD	34.90 ± 1.52

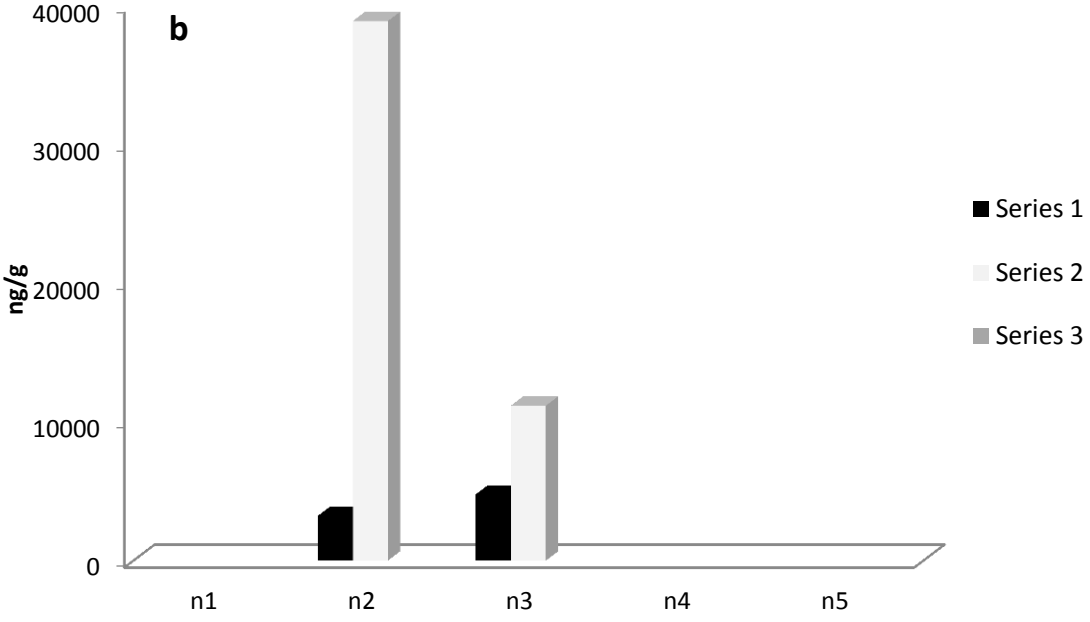

a
2: TOF MS ES+
3.61e6
MNa+
469.1107
149.0240
193.0503
341.0659
385.0918
170911_M3 2045 (7.930) Cm (2024:2054)
2: TOF MS ES+
3.61e6
MNa+
451.0997
385.0915
341.0657
149.0238
193.0502
m/z

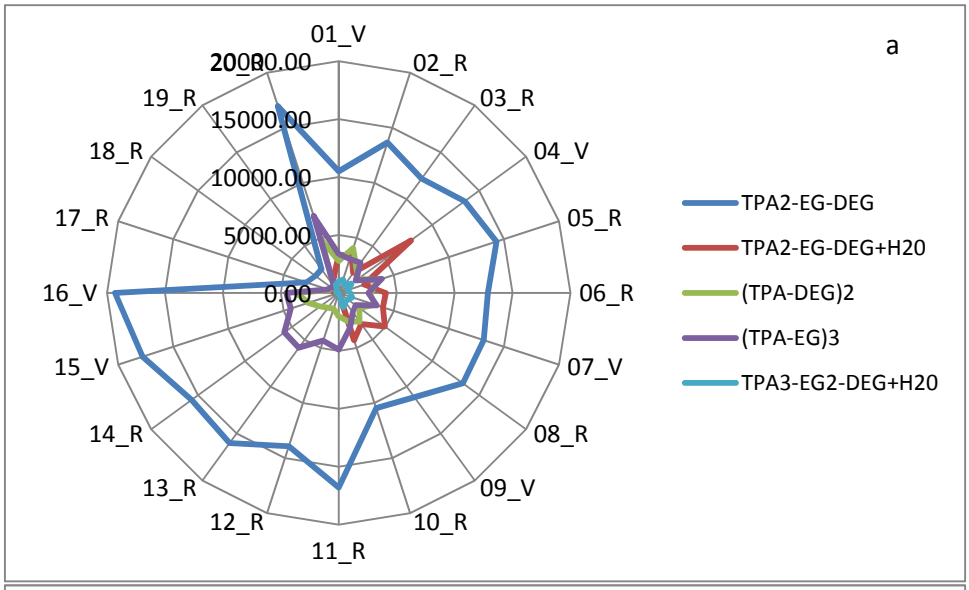

b
2: TOF MS ES+
2.41e5
MNa+
425.0836
385.0916
149.0240
193.0503
341.0660
70911_M3 2007 (7.786) Cm (1991:2013)
2: TOF MS ES+
2.41e5
MNa+
407.0738
385.0919
404.0650
190.0105
193.0502
149.0238
341.0659
m/z

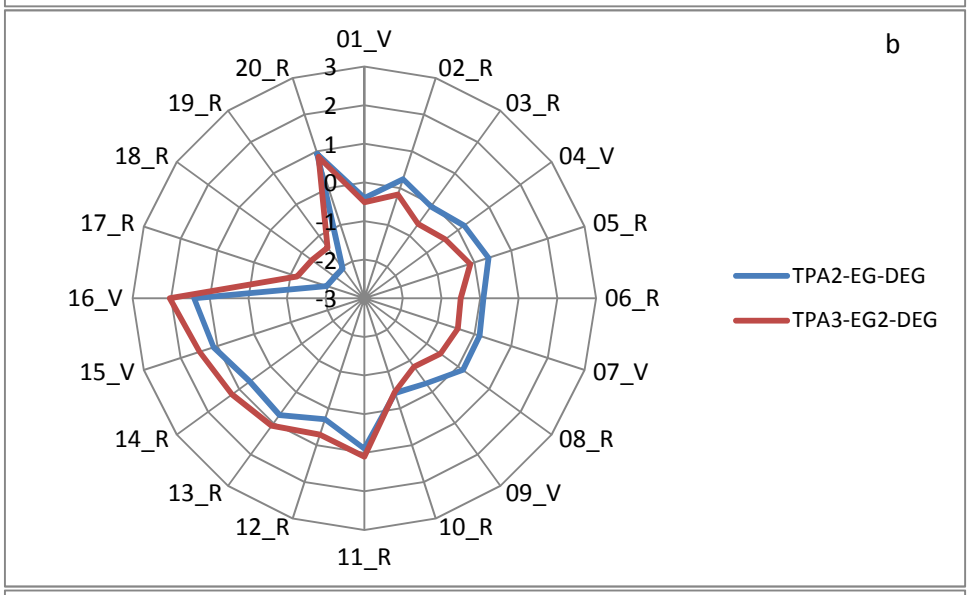
Cylic Oligomers

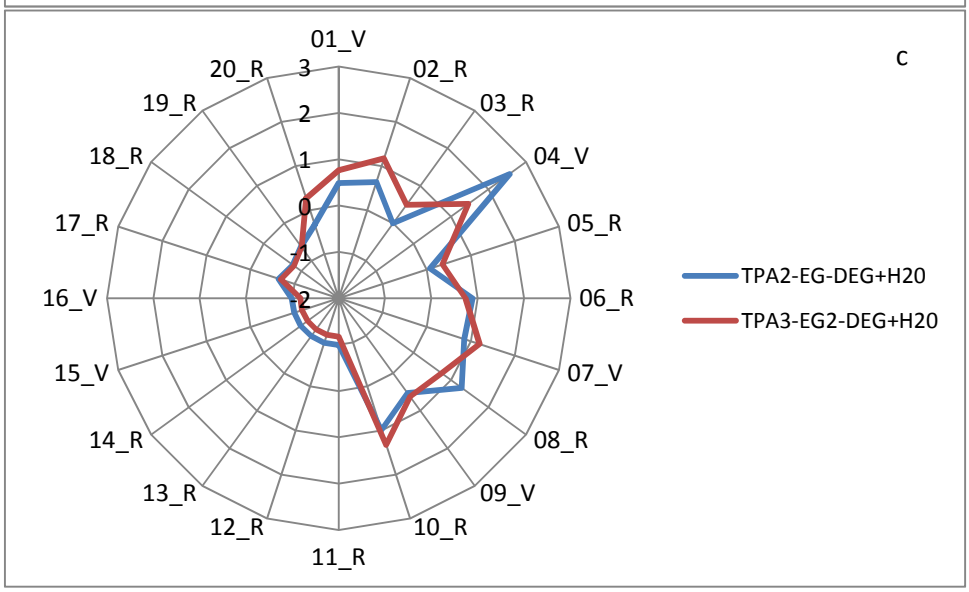


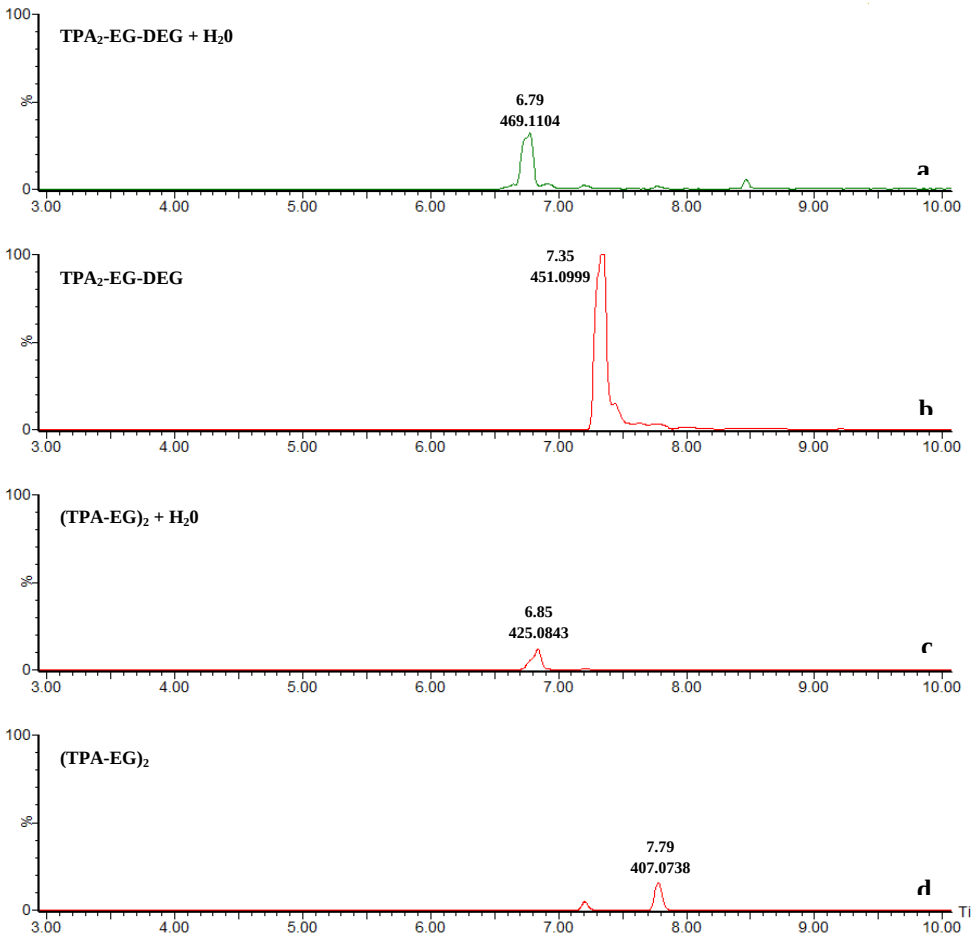
Lineal Oligomers




a
01_V
02_R
03_R
04_V
05_R
06_R
07_V
08_R
09_V
10_R
11_R
12_R
13_R
14_R
15_V
16_V
17_R
18_R
19_R
20_R
20000.00
15000.00
10000.00
5000.00
0.00
TPA2-EG-DEG
TPA2-EG-DEG+H20
(TPA-DEG)2
(TPA-EG)3
TPA3-EG2-DEG+H20


b
01_V
02_R
03_R
04_V
05_R
06_R
07_V
08_R
09_V
10_R
11_R
12_R
13_R
14_R
15_V
16_V
17_R
18_R
19_R
20_R
3
2
1
0
-1
-2
-3
TPA2-EG-DEG
TPA3-EG2-DEG


c
01_V
02_R
03_R
04_V
05_R
06_R
07_V
08_R
09_V
10_R
11_R
12_R
13_R
14_R
15_V
16_V
17_R
18_R
19_R
20_R
3
2
1
0
-1
-2
TPA2-EG-DEG+H20
TPA3-EG2-DEG+H20


TPA2-EG-DEG + H20
6.79
469.1104
a
TPA2-EG-DEG
7.35
451.0999
b
(TPA-EG)2 + H20
6.85
425.0843
c
(TPA-EG)2
7.79
407.0738
d
TPA3-EG2-DEG + H20
7.54
661.1524
e
TPA3-EG2-DEG
8.18
643.1419
f
(TPA-EG)3 +H20
7.63
617.1263
g
(TPA-EG)3
8.30
599.1158
h
%
Time
100
0
3.00
4.00
5.00
6.00
7.00
8.00
9.00
10.00