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Combined Chromatographic and Mass Spectrometric Toolbox for Fingerprinting Migration from PET Tray during Microwave Heating

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Supporting Information

ABSTRACT: A combined chromatographic and mass spectrometric toolbox was utilized to determine the interactions between poly(ethylene terephthalate) (PET) food packaging and different food simulants during microwave heating. Overall and specific migration was determined by combining weight loss measurements with gas chromatography−mass spectrometry (GC-MS) and electrospray ionization mass spectrometry (ESI-MS). This allowed mapping of low molecular weight migrants in the molecular range up to 2000 g/mol. Microwave heating caused significantly faster migration of cyclic oligomers into ethanol and isooctane as compared to migration during conventional heating at the same temperature. This effect was more significant at lower temperature at which diffusion rates are generally lower. It was also shown that transesterification took place between PET and ethanol during microwave heating, leading to formation of diethyl terephthalate. The detected migrants included cyclic oligomers from dimer to hexamer, in most cases containing extra ethylene glycol units, and oxidized Irgafos 168. ESI-MS combined with CID MS-MS was an excellent tool for structural interpretation of the nonvolatile compounds migrating to the food simulants. The overall migration was below the overall migration limit of 10 mg/dm^2 set by the European commission after 4 h of microwave heating at 100 °C in all studied food simulants.

KEYWORDS: *migration, food packaging, PET, microwave, ESI-MS*

INTRODUCTION

Migration of additives or degradation products from plastic packaging into food, when heating in a microwave oven, can cause unwanted effects such as undesirable odor coming from the food or even toxic effects. The development of analysis techniques for the detection of migrating compounds from polymers is therefore essential with regard to food safety and quality. Poly(ethylene terephthalate) (PET) is typically manufactured by polymerization of ethylene glycol and dimethyl terephthalate or terephthalic acid during a polycondensation reaction. PET has relatively low permeability to small molecules and is therefore frequently used as material for bottles containing carbonated beverages. Furthermore, due to its high-temperature stability, PET is also used in the form of trays and dishes for microwave and conventional cooking and for susceptor films. PET is known to contain low amounts of cyclic oligomers, from dimer to pentamer, at levels ranging from 0.06 to 1.0% depending on the type of PET.[1] The migration of low molecular weight compounds, such as acetaldehyde, monomers, catalysts, or degradation products, during realistic conditions of use from PET packaging into all types of foodstuffs is typically very low.[2,3]

López-Cervantes et al. found that after 7 min of heating in a 850 W microwave oven, and after 60 min of heating at 200 °C in a conventional oven, 2.7−4.1 and 2.7−3.5 mg/dm^2, respectively, of oligomers migrated from PET roasting bags into olive oil.[4] Begley and Hollifield estimated that around 65−70% of the oligomers in microwaveable PET susceptor films migrated into corn oil during a 3 min heating period in a microwave oven and that 100% migrated after a 5 min heating period when the total oligomer content was 3.7 mg/dm^2.[5] Other studies have established migration in the range from 1.4 to 4.2 mg/dm^2 into olive oil during 2 h of heating at 175 °C from PET trays of various thicknesses[6] or 0.2 mg/dm^2 into water or 15% ethanol during 1 h of heating at 95 °C.[7] Temperatures reached at the food/package interface were in the range of 61−121 °C when ready-prepared foods packaged in plastics pouches, trays, or dishes were reheated in a microwave oven.[8] PET oligomers are of low acute long- or short-term toxicity and have no specific migration limit (SML), but they are still subject to the general overall migration limit (OML) of 10 mg/dm^2 set by the European commission. Thus, the overall migration from PET packaging during one-time high-temperature migration tests typically does not exceed the overall migration limit.[9]

During microwave heating high temperatures can be reached in a short time. The use of time versus temperature profiles for the packaged food under the actual microwave cooking conditions in combination with previously established models based on package type and temperature has been suggested to predict migration during microwave heating.[10] However, the heat transfer process during microwaving is different from that during heating by conduction/convection[11] and might therefore give rise to differences in migration behavior. The package itself might also absorb microwaves and convert them into heat, which could lead to a higher temperature in the package compared to the surrounding food. This would thus lead to acceleration of any diffusion process inside the package.

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Spot heating and/or degradation can also occur during microwaving. For example, in previous work we observed that antioxidants in polypropylene packaging degraded during microwave heating in fatty food simulants, leading to increased specific migration of antioxidant degradation products, whereas the antioxidants did not degrade when the package was heated conventionally at the same temperature.[12] Microwaves also increased the diffusion rate of cyclopentanone in an epoxy resin above the rate that would be expected from the temperature alone (a so-called nonthermal "microwave effect"),[13] and a similar phenomenon was found for ethylene oxide in PVC.[14] A recent study also unequivocally established that a nonthermal microwave effect can significantly increase the rate of an organic reaction with polar reactants diluted in a nonpolar solvent.[15] Monitoring the migration from packaging into food simulants during microwave heating at controlled temperatures could therefore provide further insights into the effect of microwaves on the migration of compounds from plastics to food.

Previously, LC-MS with atmospheric pressure chemical ionization (APCI) was used to analyze degradation products in γ-irradiated PET.[16] Both LC-APCI-MS[17] and electrospray ionization mass−spectrometry (ESI-MS)[18] were utilized to analyze the extractable total oligomeric fraction in PET and for quantification of phthalates in tap water,[19] whereas high-performance liquid chromatography (HPLC) with UV detection was used to follow the migration of oligomers from PET into olive oil.[4] ESI-MS is a promising system for polymer analysis, and earlier studies have suggested that ESI ion sources can detect relatively broad ranges of product abundances.[20] Our previous studies also demonstrated the high value of ESI-MS as a tool for monitoring migration from food packaging to food stimulants[12,21] and also for analysis of polymer degradation products.[22,23]

The present study aimed at evaluating the specific effects of microwaves on the polymer−food interactions, and the aim was not to precisely simulate real use in a commercial household microwave oven. Minor factors that could affect and complicate migration in a real-world scenario such as volatilization/condensation were disregarded, and the experimental focus was put only on the transfer of migrants from package to food. The increasing microwave processing of food in society requires better understanding of the polymer−food interactions to ensure the safety and migration resistance of the microwavable polymer packages. We evaluated the interaction effects between microwavable PET trays and different food simulants during microwave heating to define the effect of microwaving in combination with different types of food. Overall migration evaluations were combined with specific migration determinations by gas chromatography−mass spectrometry (GC-MS) and ESI-MS. The potential of ESI-MS for screening the low molecular weight migrant patterns was further evaluated.

MATERIALS AND METHODS

Materials. Acetonitrile (99.9%), methanol (99.9%), and water, all of LC-MS grade, were all obtained from Fisher. This water was used for the whole study. Ethanol (99.9%) and isooctane (2,2,4-trimethylpentane) (99.0%) were obtained from Merck. Water, 10% ethanol, and 3% acetic acid were selected as food simulants in accordance with valid EU regulation (Annex III of EC 10/2011). Ethanol (at concentration >50%) and isooctane are not included in Annex III, but they have been commonly used as fatty food stimulants. In this study they were selected instead of vegetable oil as the analysis of migrants in vegetable oils is very demanding. Acetic acid (99.5%) and 2,4-*tert*-butylphenol (2,4-bis(1,1-dimethylethyl)phenol) (97%) were obtained from Acros Organics. Diethyl terephthalate (1,4-benzenedicarboxylic acid, diethyl ester) (95%) was obtained from Alfa Aesar. The black PET trays were commercial single-use trays labeled microwaveable and intended for microwave heating of food. They had a thickness of approximately 0.35 mm.

MAE and Conventional Heating Process. A MAE device was used to heat pieces of the trays in different food simulants with microwaves. The food simulants were water, 3% acetic acid, 10% ethanol, ethanol, and isooctane/ethanol. Because isooctane is nonpolar, it cannot be heated by microwaves, and therefore 10% ethanol had to be added, making a solution of 90:10 isooctane/ethanol. The MAE device was an MES-1000, a multimode microwave solvent extraction system with a rotating turntable manufactured by CEM, providing a maximum effect of 950 W. Pieces of the PET tray were cut from the trays and put into a Teflon vessel belonging to the MAE device. There were no observable differences between the two sides of the trays. The ratio between side length and edge thickness of the pieces was always above 20, which according to previous studies means that the diffusion of migrant from the edges can be neglected.[24] It was also shown experimentally that the migration of a UV stabilizer from small PET strips immersed in food simulant was equal to the migration from a whole bottle filled with food simulant.[25] Food simulant was added to the MAE vessels, covering all sample pieces. The surface area-to-volume ratio was 0.2 dm^2/10 mL. Sample vessels, containing sample pieces and food simulants, and blank samples (a vessel containing only food simulant) were heated isothermally in the MAE device for 1 h at 80 °C and for 4 h at 100 °C. The MAE operation was conducted at 50% effect for all food simulant samples except for 90:10 isooctane/ethanol samples, which were heated at full effect. For most simulants full effect (950 W) caused too rapid heating and made the temperature unstable. The temperatures were stable to limits of ±4 °C around the set temperature. The EU commission recommends that overall migration determinations for packages intended for high-temperature applications are conducted for at least 1 h.[9] The used procedures are, thus, suitable for testing of single-use microwavable packaging. However, previous studies showed that repeated microwave heating of PP packages during six 10 min intervals also resulted in approximately the same migration as 1 h of continuous heating.[26]

During conventional heating, sample pieces with food simulant were put into 20 or 100 mL glass vials, which were closed with crimp seals/screw caps with PTFE septa and put into a silicone oil bath on a heating plate set at 80 or 100 °C.

Overall Migration Determination. To determine the overall migration during microwave and conventional heating during 4 h at 100 °C, approximately 3.5 g of sample was heated in 50 mL of food simulant (surface area-to-volume ratio = 1.5 dm^2/50 mL). After the heating, three 10 mL portions of the food simulants were transferred to three preweighed 20 mL headspace glass vials. The food simulants were evaporated using nitrogen, and the vials were weighed after evaporation to determine the overall migration, which was transferred from mg to mg/dm^2 units by using the sample weights, thicknesses, and density of the trays. Density of the samples was calculated from the volume crystallinity, recalculated from differential scanning calorimetry (DSC) based weight crystallinity, and the tabulated values for 100% amorphous (1.33 g/cm^3) and 100% crystalline (1.46 g/cm^3) PET.[27] A sample density value of 1.36 g/cm^3 was calculated.

Sample Preparation for ESI-MS Analysis of the Migrants. To optimize the ESI-MS method, approximately 3.5 g of PET tray was cut into smaller pieces and put into a MAE extraction vessel together with 50 mL of ethanol. The sample was then heated for 4 h at 100 °C in the MAE device. After the heating, the vessel was allowed to cool to below 30 °C. The vessel was opened, four 10 mL portions of the ethanol were each put into a 20 mL headspace vial, and the solutions were subsequently evaporated with nitrogen until no liquid remained in the vials. One milliliter of 50:50 acetonitrile/water, 1 mL of 100% acetonitrile, 1 mL of 50:50 methanol/water, or 1 mL of 100% methanol was then added to each vial. The vials were closed with crimp caps, ultrasonicated for approximately 5 min, and stored for ESI-MS analysis.

For sample analysis an approximately 0.5 g piece of PET tray was put into 10 mL of food simulant. The heating times were 1 and 4 h. After the heating, the vessels/vials were removed from the MAE device/oil bath and left to cool to room temperature. The vessels/vials were then opened, and in the case of MAE heating, the food simulants were transferred from the Teflon vessels to 20 mL headspace glass vials. The food simulants in the vials were then evaporated by a small stream of nitrogen just above the surface of the liquid until no liquid remained in the vials. A mixture of 1 mL 50:50 methanol/water was added to each vial, and they were subsequently closed with crimp caps and ultrasonicated for approximately 5 min. The solution was thereafter filtered through a 0.45 μm PTFE filter tip. The same procedure was applied to all microwave heated and conventionally heated as well as blank control samples. The blank samples consisted of clean food simulants, which were treated according to the same heating and sample preparation procedures. These blanks were utilized to identify system impurity peaks from real migrants.

Electrospray Ionization Mass Spectrometry. Electrospray ionization mass spectra were acquired with a Finnigan LCQ ion trap mass spectrometer (Finnigan, San Jose, CA). Filtered sample solutions were directly infused into the mass spectrometer with a continuous flow of 5 μL/min. The instrument was set at positive mode, and the LCQ ion source was operated at 5 kV. The capillary temperature was set at 175 °C. Nitrogen was used as nebulizing gas, and helium was used as damping and collision gas.

Differential Scanning Calorimetry. The degree of crystallinity for original and microwave-heated samples was determined by DSC using a Mettler-Toledo DSC 820 STAR^e system with a GC100 gas controller. The heated samples were dried in a vacuum oven in room temperature to remove absorbed solvent residues before the DSC analysis. The temperature program consisted of heating from 25 to 300 °C at 10 °C/min, and then the samples were cooled from 300 to 0 °C at −10 °C/min and then heated again from 0 to 300 °C at 10 °C/min. The heating scans were performed with the sample under 80 mL/min constant nitrogen gas flow. The crystallinity was calculated with the equation

$$X_c = \frac{100 \times \Delta H_f}{\Delta H_f^0} \quad (1)$$

where X_c is the degree of crystallinity, ΔH_f is the integrated melting peak area from the thermogram divided by sample amount, and ΔH_f^0 is the melting enthalpy of a 100% crystalline polymer sample. The melting enthalpy used for 100% crystalline sample was 144.7 J/g.[27] Glass transition temperature was determined at the midpoint of the upward-sloping region in the thermograms.

Gas Chromatography–Mass Spectrometry. GC-MS analysis was conducted with a Finnigan MAT GCQ system (San Jose, CA, USA) with a Gerstel MPS2 autosampler (Mülheim an der Ruhr, Germany). The column was a wall-coated open tubular (WCOT) CP-SIL 8 CB low bleed/MS 0.25 mm × 0.25 μm × 30 m (Varian). Helium of 99.9999% purity with a constant linear velocity of 40 cm/s was used as carrier gas. The injector temperature was 250 °C, and the GC oven was programmed to 40 °C for 1 min, thereafter heating at constant rate of 10 °C/min to 270 °C and finally holding at 270 °C for 15 min. Electron ionization (EI) with 70 eV of collision energy was used, and the mass scan range was m/z 35−400. The injection volume of the directly injected samples was 1 μL, and splitless injection was performed.

Standard Solutions. A standard solution was prepared by dissolving small amounts of 2,4-*tert*-butylphenol and diethyl terephthalate in ethanol. It was used for the quantification of the analytes that migrated into the food simulants ethanol and isooctane (directly injected samples). A standard water solution of analytes for solid phase microextraction (SPME) analysis was prepared by adding 10 mL of water to a 20 mL headspace vial together with 1 μL of a chloroform solution containing the same analytes as above and letting the chloroform droplet dissolve. Diethyl terephthalate had a concentration of 6 μg/L, and 2,4-di-*tert*-butylphenol had a concentration of 1 μg/L in the standard solution.

Solid-Phase Microextraction. SPME was used to extract migrants from water before subsequent GC-MS analysis. The SPME fiber was a 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) fiber from Supelco (Bellefonte, PA, USA). It was conditioned in the injector port of the GC-MS system according to the manufacturer's instructions before usage. Ten milliliters of water solution was transferred into 20 mL headspace vials sealed with crimp seals with polytetrafluoroethylene (PTFE)/silicone septa. Extractions were carried out by penetrating the septum of the preheated vial with the fiber needle and exposing the fiber to the headspace above the solution under constant vial agitation at 500 rpm. The extraction time was 30 min, and the temperature was 80 °C. Immediately after extraction, the fiber needle was withdrawn and injected directly into the GC-MS system. The SPME extractions were carried out automatically by the Gerstel MPS2 autosampler. The compounds in the standard solution were shown to be within the linear range of the fiber.

RESULTS AND DISCUSSION

To determine the interactions between different food simulants and PET trays during microwave heating, overall migration was determined, ESI-MS was utilized to monitor the migrating PET oligomers, and GC-MS was utilized to quantify the migrated low molecular weight compounds.

Screening of Migrants by ESI-MS. During the ESI-MS screening of the migrants different ESI-MS solvents and acetic acid as protonation agent were evaluated. Spectra showing the compounds that migrated from the PET tray during heating for 4 h at 100 °C in ethanol, after redissolution in 50:50 acetonitrile/water, 100% acetonitrile, 50:50 methanol/water, and 100% methanol can be seen in Figure 1a. It shows the solvent influence related to solubility of the analytes and ion formation in the ESI-MS. The spectra obtained after the addition of 1% acetic acid can be seen in Figure 1b.

The PET oligomer peak with the highest intensity was found at m/z 879 (see Identification of PET Oligomers by ESI-MS), and therefore the intensity values for this ion were compared for the different samples. The ion at m/z 1347 was identified as the oxidized antioxidant Irgafos 168 (see Other Compounds Detected and Identified by ESI-MS), and the intensity values of this peak were also compared. The ion at m/z 702 was a system impurity peak, which was observed also during analysis of blank reference samples. The intensities of oligomer peak at m/z 879 and antioxidant peak at m/z 1347 after analysis in different solvents are shown in Figure 2. Methanol/water (50:50) resulted in the highest peak intensity for the PET oligomer ion at m/z 879 when no acetic acid was added. A higher number of other PET oligomers was also visible when 50:50 methanol/water was used as solvent, and oligomer peaks were generally stronger in this spectrum compared to the other spectra (Figure 1a). For the oxidized Irgafos 168, 100% methanol gave the highest peak, probably due to the hydrophobicity of this compound (Figure 2b). In all cases except with 100% methanol the addition of acetic acid decreased the m/z 879 peak and the rest of the PET oligomer peaks. The addition of acetic acid to the 50:50 methanol/water sample resulted in a different series of peaks, with masses that were 32 or 64 units higher than the PET oligomer peaks found in the sample without the acid (e.g., 483 instead of 451 and 943 instead of 879). These peaks could result from the addition of methanol units to the complex structures found in the other samples, that is, $[M + MeOH + Na]^+$ and $[M + 2MeOH + Na]^+$. No additional peaks corresponding to $+H^+$ adducts of the oligomers were detected in the samples with acetic acid.

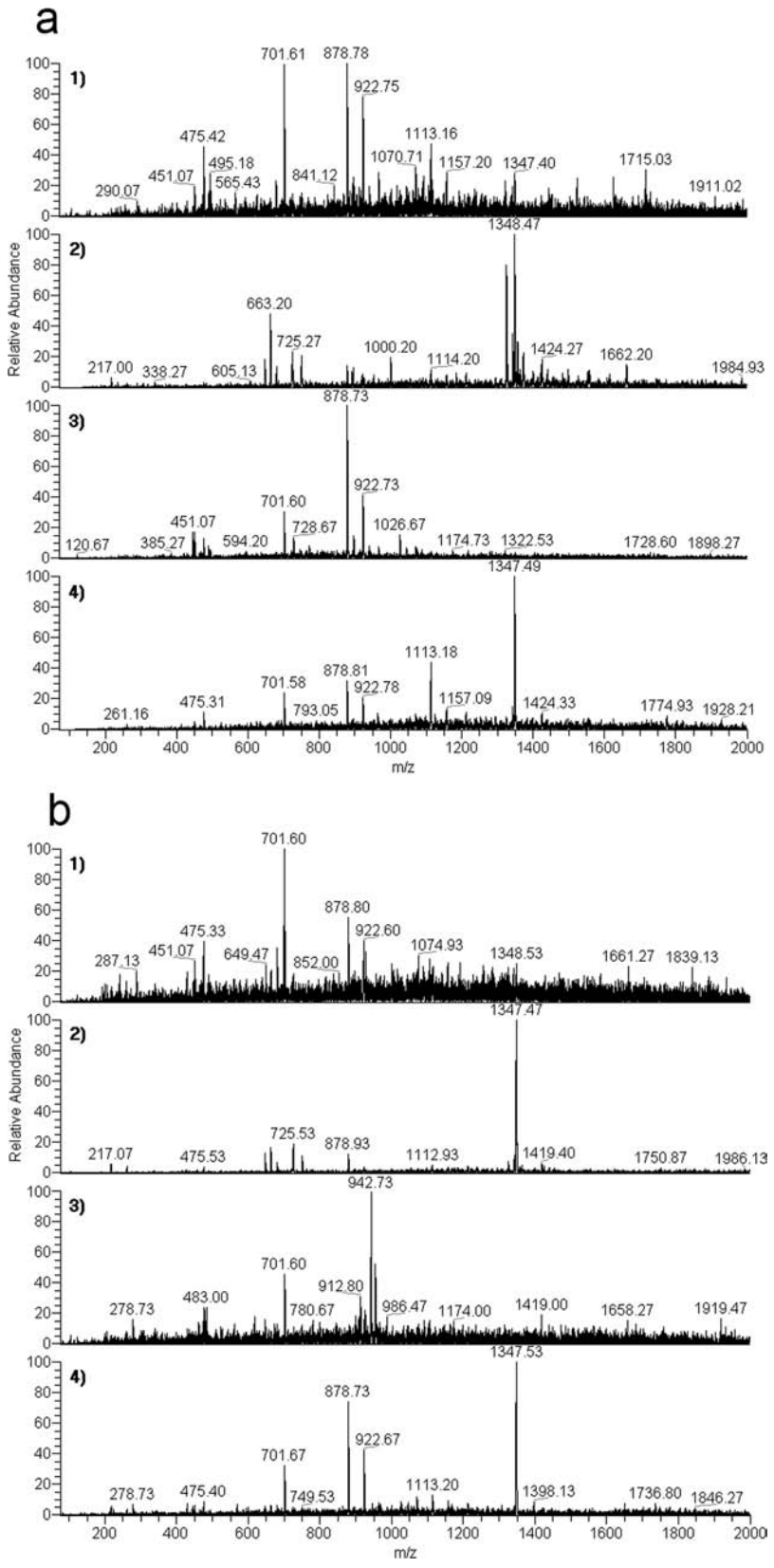

Figure 1. ESI-MS spectra from method optimization: (a) spectra without acetic acid; (b) spectra with 1% acetic acid. From top to bottom: (1) 50:50 ACN/H_2O; (2) 100% ACN; (3) 50:50 MeOH/H_2O; (4) 100% MeOH.

Identification of PET Oligomers by ESI-MS. Table 1 summarizes the strongest peaks from the ESI-MS spectra of migrants in ethanol and shows some structural assignments of the peaks. All peaks in the table are single-charged, as was seen from their isotope peaks. The peaks were assigned as cyclic PET oligomers because the m/z values (minus the adduct)

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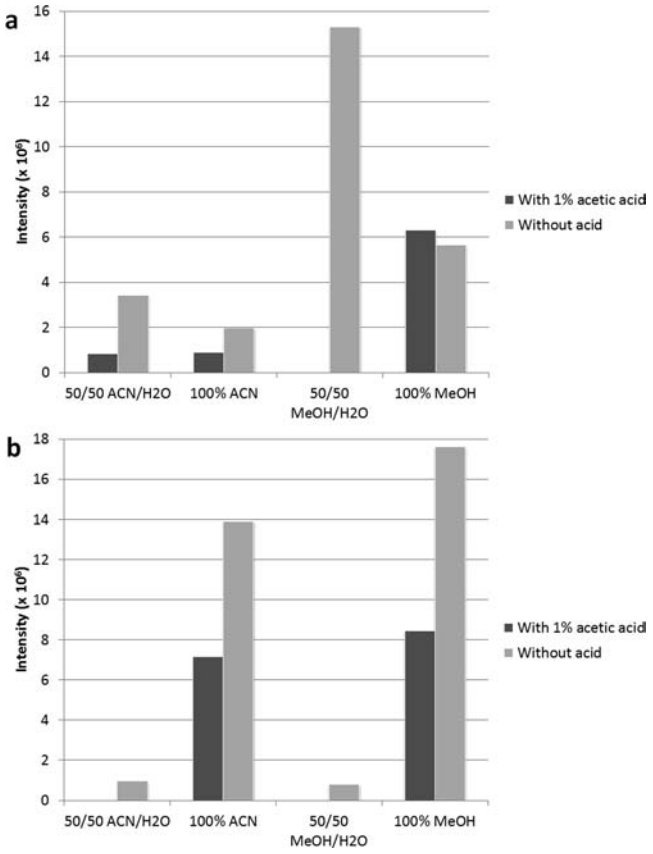

Figure 2. Comparison of ion intensity values for PET oligomer ion at m/z 879 (a) and oxidized Irgafos 168 ion at m/z 1347 (b) in different ESI-MS solvents with and without acetic acid.

correspond to $192n + 44m$, where m and n are integers, 192 is the molecular weight of the repeating unit, and 44 is an additional ethylene glycol (EG) unit. The high temperature and acid conditions during PET polymerization can cause the formation of traces of diethylene glycol (DEG) from ethylene glycol units.[17] The replacement of an EG unit with a DEG unit in the chain results in an increase in molecular weight by 44 amu (one EG). This series of oligomers has earlier been observed both in commercial PET samples[18] and in bottle grade PET (obtained from manufacturers).[17] Holland et al. also utilized ESI-MS to analyze the oligomers present in PET samples, and oligomer series from monomer to pentamer containing one to two extra EG units were detected.[18] The highest intensity peak in their ESI-MS analysis belonged to the $[PET]_2[EG] + Na^+$ (m/z 451) oligomer adduct. Our study shows that these oligomers migrate to ethanolic food simulants during heating of PET.

The cyclic trimer usually constitutes the largest fraction of the different oligomers present in PET. López-Cervantez determined by semiquantitative HPLC-UV analysis using a cyclic trimer as standard that the cyclic trimer constituted more than half of the total oligomeric content in PET roasting bags for microwave applications (5.58 mg/dm^2 of a total of 8.71 mg/dm^2).[4] In our study no trimers were seen as molecular ions; instead, trimer fragments were observed in a few cases after collision-induced dissociation (CID) fragmentation (Table 1). The lack of observation of any PET trimers in the spectra leads to the possibility that some of the reported ions with more than four PET monomer units could be complex double-molecular adducts composed of one trimer plus one dimer or higher oligomer. Because the complex adduct of, for example, one dimer and one trimer would appear at the same peak in the spectra as one pentamer, these should be very difficult to distinguish by direct infusion ESI-MS. Harrison showed that cyclic PET oligomers higher than trimer undergo fragmentation by neutral losses of cyclic trimers during CID MS-MS and, as a result, tetramers were found to primarily

Table 1. Peak Assignments from ESI-MS Analysis of the Compounds Migrating from PET into Ethanol during Heating Together with MS-MS Fragment Peaks (m/z)

	structure[a]	MS-MS fragment peaks[a]
PET oligomer[b]		
446	$[PET]_2[EG] + H_2O^+$	
451	$[PET]_2[EG] + Na^+$	385 ($[PET]_2 + H^+$), 341 ([PET][TA] + H^+), 193 ([PET] + H^+)
490	$[PET]_2[EG]_2 + H_2O^+$	
495	$[PET]_2[EG]_2 + Na^+$	
879	$[PET]_4[EG]_2 + Na^+$	451 ($[PET]_2[EG] + Na^+$)
897	$[PET]_4[EG]_2 + H_2O + Na^+$	469 ($[PET]_2[EG] + H_2O + Na^+$), 495 ($[PET]_2[EG]_2 + Na^+$)
923	$[PET]_4[EG]_3 + Na^+$	535, 495 ($[PET]_2[EG]_2 + Na^+$), 451 ($[PET]_2[EG] + Na^+$)
941	$[PET]_4[EG]_3 + H_2O + Na^+$	429 ($[PET]_2[EG] + H^+$), 451 ($[PET]_2[EG] + Na^+$), 469 ($[PET]_2[EG] + H_2O + Na^+$), 495 ($[PET]_2[EG]_2 + Na^+$), 513 ($[PET]_2[EG]_2 + H_2O + Na^+$), 685 ($[PET]_3[EG]_2 - 2H + Na^+$)
1027	$[PET]_5[EG] + Na^+$	451 ($[PET]_2[EG] + Na^+$), 599 ($[PET]_3 + Na^+$)
1071	$[PET]_5[EG]_2 + Na^+$	495 ($[PET]_2[EG]_2 + Na^+$), 643 ($[PET]_3[EG] + Na^+$), 451 ($[PET]_2[EG] + Na^+$)
1175	$[PET]_6 + Na^+$	
1219	$[PET]_6[EG] + Na^+$	
other compounds		
663[c]	$[IGF] + H^+$	
1325[c,d]	$2[IGF] + H^+$	
1342[c,d]	$2[IGF] + H_2O^+$	
1347[c,d]	$2[IGF] + Na^+$	

[a]Abbreviations: PET, polyethylene terephthalate repeating unit (mol weight, 192); EG, ethylene glycol unit (mol weight, 44); TA, terephthalic acid unit (mol weight, 148); IGF, oxidized Irgafos 168 (mol weight, 662). [b]Detected using 50:50 methanol/water as solvent. [c]Detected using 100% acetonitrile as solvent. [d]Detected using 100% methanol as solvent.

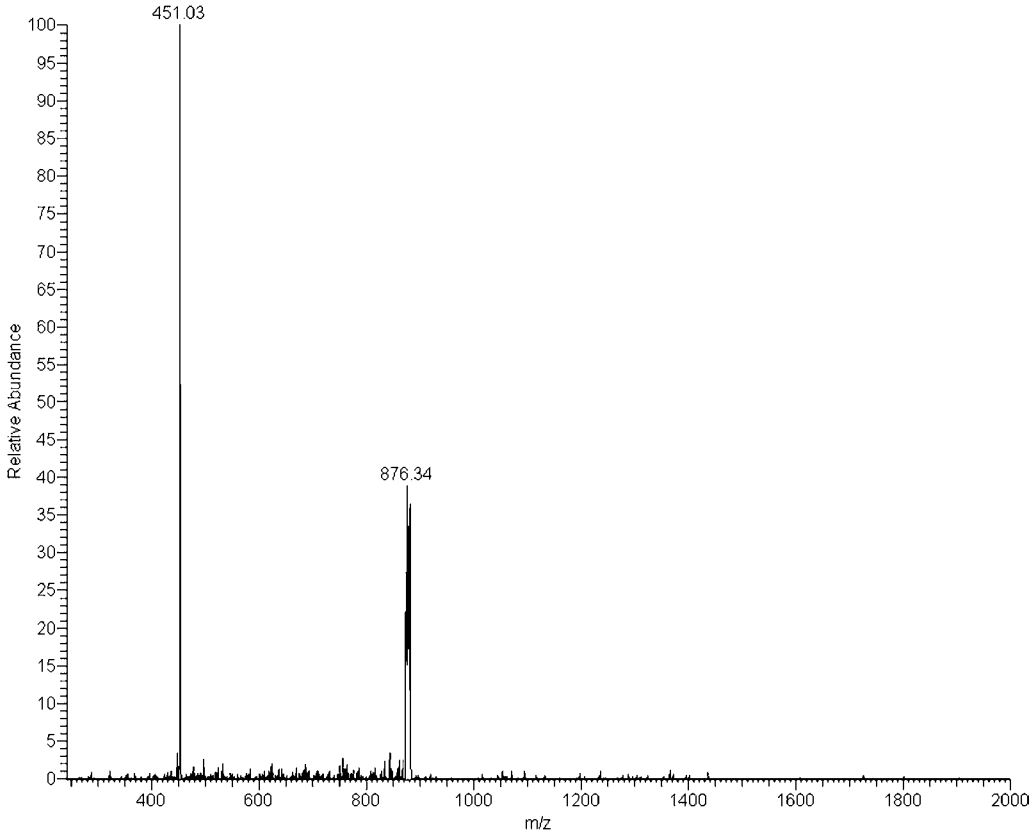

Figure 3. MS-MS analysis of the PET tetramer ion at m/z 879 using 20% collision energy showing the fragmentation into the PET dimer at m/z 451 ($[PET]_2[EG] + Na^+$).

fragment into monomers.[28] Double-molecular adducts have, for example, been observed in ESI-MS spectra during analysis of sulophenem prodrugs.[29] Fragments with structural assignments for some of the peaks are given in Table 1. Figure 3 shows one example of fragmentation of m/z 879 to 451; that is, no trimer was leaving group or fragment. However, if the m/z 879 peak was a double-molecular adduct of two dimers, this fragmentation pattern would be expected because the cleavage would be primarily at the weak ionic bonds. Structural assignments of the fragments from the $[PET]_2[EG] + Na^+$ peak are shown in Figure 4. It shows that this dimer primarily cleaves at the carbon−oxygen bond next to an EG unit.

Other Compounds Detected and Identified by ESI-MS. A large peak was found at m/z 1347 when 100% acetonitrile or methanol was used as solvent, and this peak was accompanied by additional peaks at m/z 1342 and 1325 (Table 1 and Figure 1a). This series probably results from $+H^+$, $+H_2O^+$, and $+Na^+$ adducts of the same compound. On the basis of the CID MS-MS fragmentation pattern (Figure 5), this compound was identified as the double-molecular ion ($[2M + adduct]^+$) of oxidized Irgafos 168 (CAS Registry No. 95906-11-9) with the nominal molecular weight of 662 ($C_{42}H_{63}O_4P$). The oxidized Irgafos 168 was previously found to have a MS-MS fragmentation pattern with the same m/z values (383, 439, 495, 551, 607, and 663) in thermal desorption mass spectrometry.[30] A peak was also observed at m/z 663, assigned as the $[M + H]^+$ adduct of oxidized Irgafos 168 using 100% acetonitrile as ESI-MS solvent (Table 1 and Figure 1a). The pattern in Figure 5 results from the losses of the six *tert*-butyl groups followed by proton transfer. Further support for the identification of these peaks as oxidized Irgafos 168 is found from GC-MS analysis, which showed the migration of the Irgafos 168 degradation product, 2,4-di-*tert*-butylphenol from the PET tray (see GC-MS Analysis of Low Molecular Weight Migrants).

Comparison of ESI-MS Analysis with Overall Migration. In Table 2 the overall migration values after 4 h of microwave heating at 100 °C in water, 3% acetic acid, 10% ethanol, and ethanol and isooctane are listed. It is also noted whether oligomer migration was detected by ESI-MS in the various food simulants. Figures 6 and 7 show spectra of the migrants after microwave and conventional heating for 1 h at 80 °C and for 4 h at 100 °C in ethanol. As shown by Table 2 and Figure 7, oligomers migrated into ethanol and 90:10 isooctane/ethanol during 1 h of microwave heating at 80 °C, but not during conventional heating for 1 h at 80 °C. In Figures 6 and 7 the peaks at m/z 451, 879, 923, 1027, and 1071 all result from PET oligomers (see Identification of PET Oligomers by ESI-MS). After 4 h of microwave and conventional heating at 100 °C, oligomers migrated into ethanol, and the relative peak intensities of the oligomer peaks were only slightly higher for the microwave-heated samples compared to the conventionally heated samples. After 4 h of microwave heating at 100 °C, oligomers migrated into isooctane/ethanol 90:10, but only weak oligomer signals at m/z 451 and 879 were observed after conventional heating for 4 h at 100 °C in 90:10 isooctane/ethanol. Overall migration values after 4 h of heating at 100 °C were all below the EU commission overall migration limit of 10 mg/dm^2.[9]

The fact that oligomers were detected after microwave heating for 1 h at 80 °C but not after conventional heating for 1 h at 80 °C and that oligomer peaks generally were more

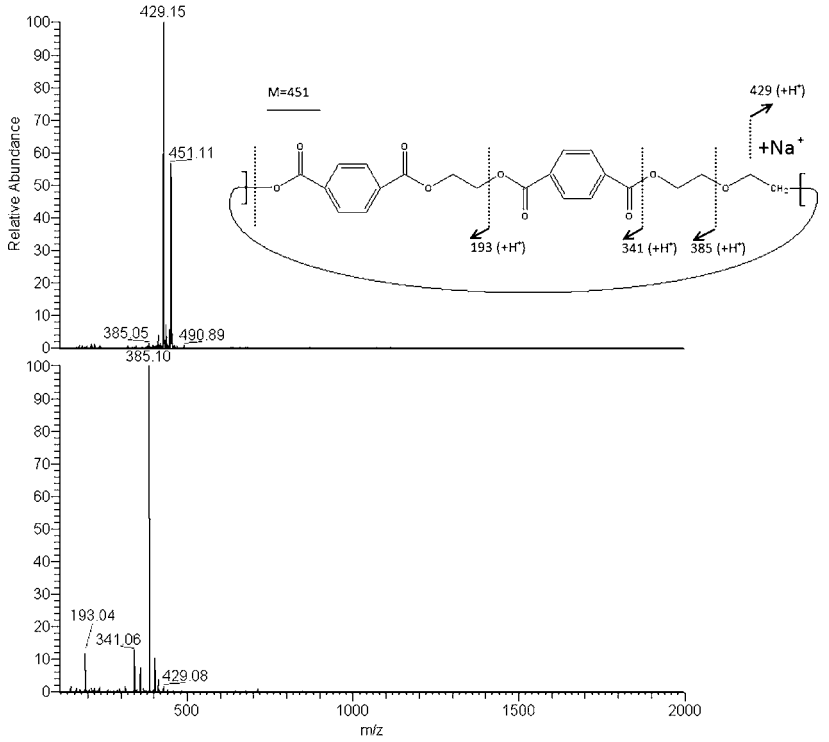

Figure 4. ESI-MS-MS spectra for the ion at *m/z* 451. The ion at *m/z* 451 corresponds to the sodium adduct of the PET dimer. Fragment peaks with neutral losses followed by proton transfer are shown, after application of 30% collision energy (top spectrum) and after application of 40% collision energy (bottom spectrum). The MS-MS fragmentation pattern is also shown in the scheme.

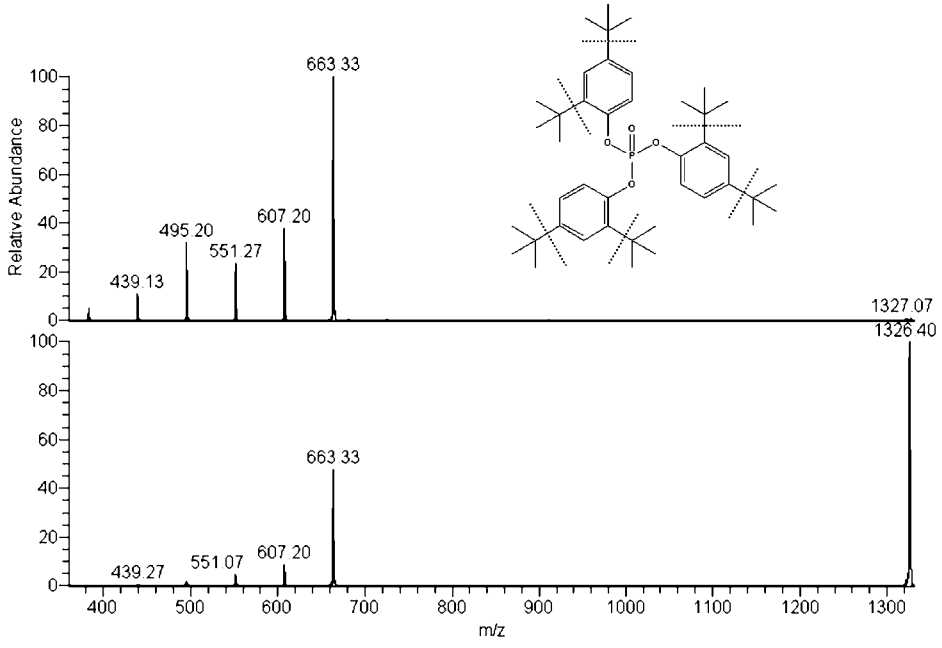

Figure 5. MS-MS spectra for the ion at *m/z* 1325, identified as oxidized Irgafos 168. Several peaks with 56 amu (C_4H_8) difference could be observed (*m/z* 383, 439, 495, 551, 607, 663) corresponding to neutral losses of the *tert*-butyl groups, each followed by proton transfer. (Top) After application of 40% collision energy. (Bottom) After application of 20% collision energy.

intense after 4 h of microwave heating at 100 °C compared to after conventional heating for 4 h at 100 °C could probably be due to a nonthermal "microwave effect",[13] which could increase the diffusion of cyclic oligomers in the polymer. No such effect was earlier observed when the migration of a trimer from PET susceptor packaging was compared to predicted values from the time versus temperature profile during microwave heating;[10] however, the temperatures in those experiments ranged from 120 to 200 °C. At such high temperatures any microwave effect would probably be insignificant. In this study almost similar overall migration values were measured at the higher temperature of 100 °C, and oligomers were detected after both microwave and conventional heating at this temperature, also suggesting that the microwave effect is more significant at

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Table 2. Migration from the PET Tray into Various Food Simulants during Microwave (MW) and Conventional (conv) Heating[a]

	water	3% ac	10% ethanol	ethanol		isooctane/ethanol 90:10		isooctane
heating time, temperature, type of migration	MW	MW	MW	MW	conv	MW	conv	conv
1 h, 80 °C								
ESI-MS (oligomers)	ND	ND	ND	D	ND	D	ND	
4 h, 100 °C								
ESI-MS (oligomers)	ND	*b*	*b*	D	D	D	*b*	ND
overall migration (mg/dm^2)	0.13 ± 0.87	0.69 ± 0.91[c]	0.72 ± 0.0	4.8 ± 2.2[c]	4.5 ± 3.4	3.6 ± 1.4[c]	2.0 ± 0.3[c]	3.2 ± 1.1[c]

[a]Overall migration values are given as the mean ± standard deviation from three replicates. MW, microwave; conv, conventional; D, detected; ND, not detected. [b]Only oligomer ions at m/z 451 and 879 were detected with weak signals. [c]Significant difference ($p < 0.05$) between the values of sample and reference blank.

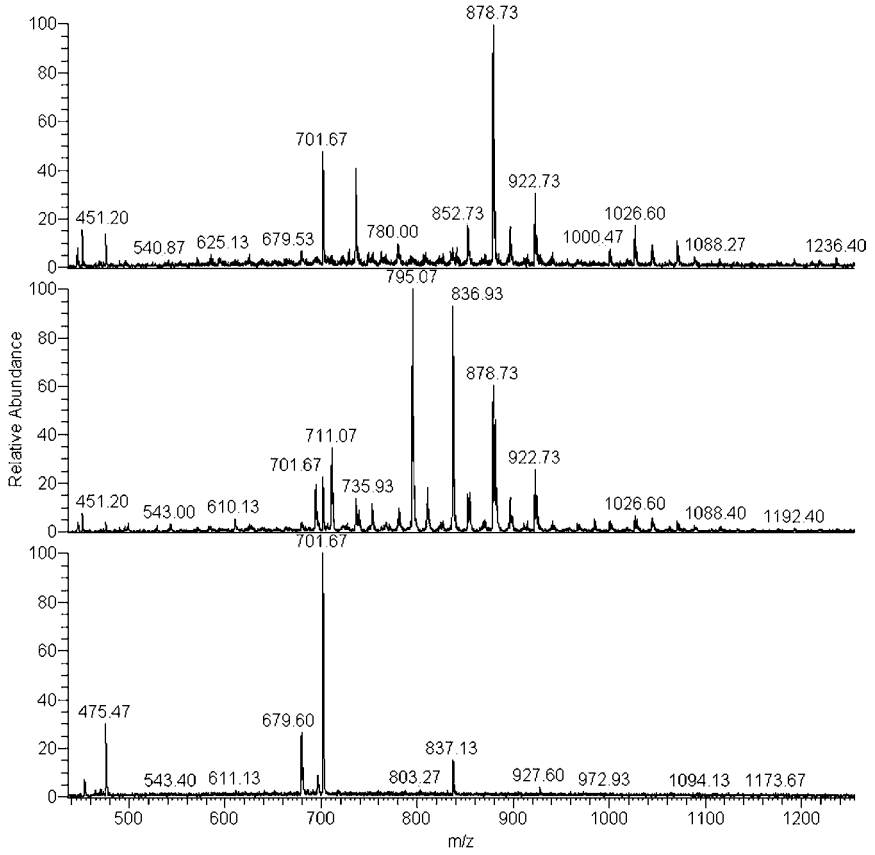

Figure 6. ESI-MS spectra of the migrants from PET microwave heated for 4 h at 100 °C in ethanol (top), from PET conventionally heated for 4 h at 100 °C (middle), and from a blank reference sample microwave heated for 4 h at 100 °C (bottom).

lower temperatures. It was also interesting that only weak oligomer signals were observed after 4 h of conventional heating at 100 °C in isooctane/ethanol, whereas all of the oligomer peaks were clearly visible after 1 h of microwave heating at 80 °C in the same simulant. The fact that the migration was seemingly larger even after microwaving at the much lower temperature and during a shorter time suggests a rather significant microwave effect. There were noticeably more visible residues (white precipitate) in the evaporated microwave-heated ethanol and isooctane food simulant samples in comparison with the corresponding conventionally heated samples.

Mathematical modeling can also be used to estimate migration in cases when the initial concentration of compounds is known. This can be done, for example, by using the EU recognized diffusion model for estimation of migration into foodstuffs.[31] The cyclic trimer has usually been reported to be the most abundant cyclic oligomer species present in PET,[4] whereas the total oligomer content can be as high as 1%.[1] The initial oligomer concentration was not known in this study, but assuming a rather extreme case of 1% oligomer content, of which the trimer constitutes 80%, and furthermore assuming high solubility in the food simulant (a polymer/food simulant partition coefficient of 1), the calculated migration of the trimer after 4 h at 100 °C is 0.7 mg/dm^2. This figure is quite low compared to the overall migration values determined into ethanol and isooctane, even if the migration of other PET oligomers is taken into account. The content of other additives in the PET sample is also expected to be low. Interaction with the food simulant, causing swelling of the polymer, might therefore partly explain the higher overall migration values observed. For example, heating in ethanol was earlier shown to

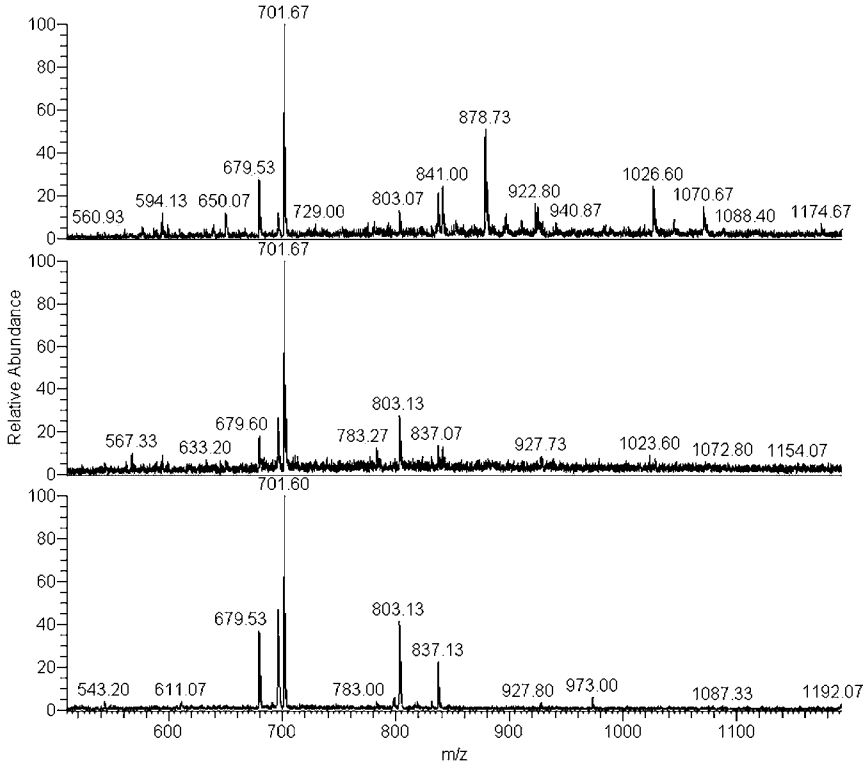

Figure 7. ESI-MS spectra of the migrants from PET microwave heated for 1 h at 80 °C in ethanol (top), from PET conventionally heated for 1 h at 80 °C (middle), and from a blank reference sample microwave heated for 1 h at 80 °C (bottom).

Table 3. Migration of Low Molecular Weight Compounds from PET during Microwave Heating in Ethanol

RT (min)	compound	CAS Registry No.	water 1 h, 80 °C (mg/dm^2)	ethanol 1 h, 80 °C (mg/dm^2)	isooctane/ethanol 1 h, 80 °C (mg/dm^2)	ethanol 4 h, 100 °C (mg/dm^2)
14.6	2,4-bis(1,1-dimethylethyl)phenol	96-76-4	ND[a]	0.0007	ND	0.016
16.4	1,4-benzenedicarboxylic acid, diethyl ester-	636-09-9	ND	ND	ND	0.033

[a]ND, not detected.

result in higher diffusion coefficient compared to heating in isooctane for the migration of an UV stabilizer from PET.[23] This was explained by stronger polymer−food simulant interaction, and the same phenomenon might also explain the somewhat higher overall migration into ethanol compared to isooctane/ethanol in our study. The PET oligomers are also more soluble in ethanol than in isooctane due to the ester groups.

GC-MS Analysis of the Low Molecular Weight Migrants. Migrants detected in water, ethanol, and isooctane/ethanol 90:10 after 1 h of microwave heating of PET and food simulants at 80 °C and in ethanol after 4 h of microwave heating at 100 °C are summarized in Table 3. Increased migration of the diethyl ester of 1,4-benzenedicarboxylic acid (diethyl terephthalate) was observed as a function of longer heating time and temperature. The diethyl terephthalate can be formed by a transesterification reaction between the polymer chains and ethanol, or it could be a side product formed during polymerization. The migration of 2,4-bis(1,1-dimethylethyl)phenol also increased with time and temperature. This compound is a well-known degradation product from the antioxidant Irgafos 168, which is commonly present in polyolefin plastic packages, but has also been identified as a migrant from PET packaging.[12,32] Its oxidized form was also detected during the ESI-MS analysis. No compounds were detected in water after 1 h of microwave heating at 80 °C. Diethyl terephthalate had a detection limit of 8 ng/L (0.4 ng/dm^2) and 2,4-di-*tert*-butylphenol a limit of 0.1 ng/L (0.005 ng/dm^2) in water.

To confirm the origin of diethyl terephthalate migrating from the samples, that is, whether it was formed during heating in ethanol or originally present in the polymer, a sample was also microwave heated for 1 h at 100 °C in pure methanol. The extract was subsequently analyzed with GC-MS. A large peak for dimethyl terephthalate was observed in the resulting chromatogram, but no peak corresponding to diethyl terephthalate could be found. If diethyl terephthalate was originally present in the PET tray, it would have been visible in the chromatogram because the solubility of diethyl terephthalate in methanol is high. Consequently, the diethyl terephthalate migrating during the heating in ethanol was formed during the microwave heating due to transesterification reaction with ethanol.

DSC Analysis and Food Simulant Sorption after Heating in Food Simulants. The PET tray originally had a glass transition temperature of 79 or 80 °C as determined from the first or second heating scan, respectively. The heating in food simulants did not influence the glass transition temperature. The crystallinity of the samples before and after heating in the different food simulants is given in Table 4.

Table 4. DSC Analysis (Crystallinity, Percent) of PET Samples before and after Microwave Heating in Different Food Simulants, Taken from the First/Second Heating Scan

heating time, temp	original	90/10 isooctane/ethanol	ethanol	10% ethanol	3% acetic acid	H_2O
1 h, 80 °C	24/24	23/23	24/24	25/23	24/24	24/24
4 h, 100 °C			22/23			

The crystallinity was not altered by heating in the food simulants for 1 h at 80 °C. The stronger interaction with ethanol was also seen as slightly higher sorption values during both microwave and conventional heating for 1 h at 80 °C (Figure 8) and the increased migration of the diethyl

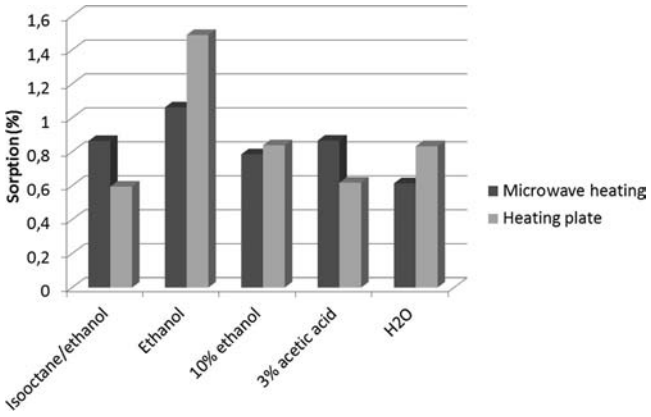

Figure 8. Sorption of the different food simulants after microwave and conventional heating for 1 h at 80 °C.

ester of 1,4-benzenedicarboxylic acid (diethyl terephthalate) during heating for 4 h at 100 °C compared to heating for 1 h at 80 °C (Table 3). This interaction could make ethanol unsuitable as a food simulant for PET during microwave heating.

In conclusion, microwave heating clearly increased the migration of cyclic oligomers from the PET tray to food simulants. The migration into ethanol and isooctane/ethanol 90:10 was significantly higher during microwave heating compared to conventional heating at the same temperature. The effect of microwaves was also more significant at the lower heating temperature of 80 °C, indicating a more significant microwave effect at lower temperatures, whereas diffusion rates at higher temperatures are generally higher. Due to ethanol's stronger interaction with PET and expected higher solubility of the PET oligomers, overall migration was larger into ethanol compared to the other studied food simulants. Furthermore, PET chains underwent transesterification with ethanol during microwave heating to a minor degree, resulting in the formation and subsequent migration of diethyl terephthalate. ESI-MS combined with CID MS-MS proved to be greatly useful for the structural interpretation of the unvolatile compounds migrating to the food simulants.

■ ASSOCIATED CONTENT

Supporting Information

Additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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