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Citation for published version (APA):
Hoppe, M., Fornari, R., de Voogt, P., & Franz, R. (2017). Migration of oligomers from PET: determination of diffusion coefficients and comparison of experimental versus modelled migration. *Food additives & contaminants. A, 34*(7), 1251-1260. https://doi.org/10.1080/19440049.2017.1322222

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Migration of oligomers from PET: determination of diffusion coefficients and comparison of experimental versus modelled migration

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ABSTRACT

Polyethylene terephthalate (PET) is increasingly used as food-contact material in, for example, containers for beverage such as bottles for soft drinks, mineral water, juices and beer. Mass transport of substances present in packaging materials into the packed food and beverages is monitored to verify the food law compliance of the materials. PET is known to contain or give rise to migrants that are oligomers derived from the polymeric material. Until now their actual migration potential has been investigated only poorly. A convenient way to determine their migration would be by using models. To verify existing models with experimental data, a migration kinetic study of PET oligomers was conducted. PET bottle material was submerged in 50% ethanol at 80°C for 15 h. The oligomer content in the migration solutions was determined every hour using LC-MS with the first-series cyclic PET trimer as standard. Diffusion coefficients of five PET oligomers (first-series dimer and trimer, second-series dimer and trimer, and third-series dimer) were calculated from the obtained data and compared with the calculated diffusion coefficients using the models of Welle and Piringer. This is the first study to provide diffusion characteristics of oligomers in PET other than the first-series cyclic trimer.

Introduction

Polyethylene terephthalate (PET) is used as a food-packaging polymer for numerous applications, which include bottles for soft drinks, mineral water, juices and beer, flexible packaging films, and microwave containers. As with other food-contact polymers, low molecular weight constituents can be transferred from the polymer into food under the conditions of use, a process that is generally denoted as 'migration'. PET is known to be one of the most inert food-contact polymers, which shows generally low migration (Störmer et al. 2004), and acts as an efficient functional barrier against organic molecules. Substances known to migrate from PET into beverages and food simulants include acetaldehyde (Ewender et al. 2003), the acetaldehyde scavenger 2-aminobenzamide (Franz et al. 2016), antimony (Welle & Franz 2011), UV-blocking additives (Begley et al. 2004), and oligomers (Begley et al. 1990; Gramshaw & Soto-Valdez 1998; Heimrich

et al. 2015). In the latter case, these migrants may be formed during the manufacturing process by incomplete polymerisation, thermal or hydrolytic degradation of polymer chains during (re)processing, or due to conditions of use. In PET polymer, cyclic oligomers from the dimer to the heptamer but also linear oligomers have been detected (Kim & Lee 2012a). Two series of oligomers with distinct molecular compositions have been identified (Barnes et al. 1995): the first series comprises an equal number of terephthalic acid and ethylene glycol units, whereas in the second series one monoethylene glycol unit is replaced by a diethylene glycol. A third series, in which two monoethylene glycol units are replaced by two diethylene glycol units, can also be formed (Holland & Hay 2002). The second and third series of oligomers arise due to the unwanted co-monomer diethylene glycol, which is a by-product during PET production.

PET oligomers can migrate at higher temperatures into fatty foods (like pizza, French fries and

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popcorn), leading to concentrations of 0.02–2.73 mg kg^{-1} (Castle et al. 1989) and 0.12–6.45 µg g^{-1} (Begley et al. 1990). Also, migration into oil was found after microwave heating under different conditions, e.g., from PET microwavable trays into corn oil at 0.167 mg in^{-2} (2.6 mg dm^{-2}), which represented 70.8% of the total oligomer content present in the PET material (Begley & Hollifield 1990b). In another study, oligomers migrated from PET roasting bags into olive oil at 2.7–4.1 mg dm^{-2} (López-Cervantes et al. 2003), which was between 31% and 47% of the total oligomer content. These oligomers are also known to migrate at lower temperatures into beverages at much lower levels of 0.05–0.47 mg kg^{-1} (Castle et al. 1989) and food simulants (Kim & Lee 2012b). Overall, depending on the food simulant and time and temperature conditions, the migration of oligomers was found to vary between 0.23 and 42.02 µg dm^{-2}.

Regulation (EU) No. 10/2011 on plastic materials intended to come into contact with food does not specifically regulate the levels of oligomers in general (European Union 2011). Therefore, in the past any restrictions on oligomer migration were assumed to be covered by the overall migration limit, which is 10 mg of total constituents released per dm^2 food-contact surface. The reported levels of PET oligomer migration are all far below this migration limit. However, two EFSA opinions, published in 2014, concerning new co-monomers for polyester food-contact materials, specified a limit of 50 µg kg^{-1} for total oligomer migration (EFSA 2014a, 2014b). The two co-monomers and the restriction of their oligomer migration are listed in the recent 6th Amendment 1416/2016 of Regulation (EU) No. 10/2011. It is noteworthy that if the same restrictions were applied to PET oligomers in general, some of the reported migration levels would exceed this limit of 50 µg kg^{-1}.

Protection of consumer health requires that food-contact materials meet the specific regulated standards for migration and, in any case, the requirement of Article 3 of the Framework Regulation (EC) No. 1935/2004 (European Union 2004). Food is packed and stored under different conditions, and it would be difficult if not impossible to investigate all these conditions in detail. Therefore, the prescribed legal testing methods for food-contact plastics involve the use of food simulants under defined temperature and time storage conditions, which should make

migration testing more convenient, the results more comparable and simplify risk assessment. Migration modelling, another legally recognised migration-evaluation approach, which is based on the compositional analysis of the food-contact material, saves even more time and resources. Only the initial concentration of the migrant of interest in the material needs to be determined, and, in combination with the respective diffusion coefficient of the migrant in the particular polymer, that value, once measured or otherwise known, can be used to calculate the migration for any time–temperature set of conditions. To do so, the diffusion coefficient of a specific migrant in the polymer at the applied test temperature has to be known. The diffusion coefficient can either be experimentally determined or estimated by mathematical models. Two models are currently used: one more universal model (Piringer et al. 1998) and another specifically developed for PET (Welle 2013). Both models are based on various experimental observations.

Migration evaluation of oligomers is a subject of increasing interest and relevance since these oligomers are polymer-accompanying substances that are virtually always present in food-contact polymers and which need to be included in risk assessments. It would therefore be advantageous to know about their migration behaviour to model the possible exposure of the consumer. Part of this undertaking has already been reported by Begley and Hollifield: for the major PET oligomer, the first-series cyclic trimer, diffusion coefficients at three different temperatures into olive oil were determined (Begley & Hollifield 1990a).

The objective of the present study was to measure the migration of this and additional PET oligomers under somewhat exaggerated test conditions and to determine in this way experimentally the diffusion coefficients for the individual molecules. For cross-validation the values derived experimentally should be compared with the diffusion coefficients calculated using both the abovementioned modelling approaches. The experimental and calculated values were compared to determine the accuracy of theoretical migration models in terms of their ability to predict the migration of PET oligomers. To the best of our knowledge, diffusion coefficients for PET oligomers other than the PET first-series cyclic trimer have not been determined thus far.

Materials and methods

Materials and reagents

All reagents and solvents were of analytical quality. Virgin PET bottles were provided by a PET bottle manufacturer. The bottle wall thickness was 0.025 cm; the density of the material was 1.52 g cm^{-3}. The PET first-series cyclic trimer (3,6,13,16,23,26-hexaoxatetracyclo[26.2.2^{8,11}.2^{18,21}] hexatriaconta-1(30),8,10,18,20,28,31,33,35-nonaene-2,7,12,17,22,27-hexone; CAS No. 7441-32-9) was obtained from Santa Cruz Biotechnology (Heidelberg, Germany).

Determination of oligomer concentration in the material

To detect PET oligomers and determine their total concentration in the PET material, 10-g samples of the bottle wall were ground at 18,000 rpm using an ultracentrifugal mill (cooled with liquid nitrogen) fitted with a 750-µm holed sieve. We extracted 2.5 g of the resulting powder with 5 ml dichloromethane in a glass vial for 7 days at 40°C, followed by ultrasonic treatment for 1 h. The extract was passed through a 0.22-µm PTFE filter and diluted in acetonitrile for LC-MS analysis. A second extraction (post-extraction) was conducted following the same procedure.

Determination of migration into 50% ethanol

To determine the migration kinetics, the PET material was cut into strips (5 × 1 cm) and five strips were extracted with a Büchi Speed Extractor at 80°C. The extraction cells were filled with 20 ml 50% ethanol at a pressure of 100 bar. The liquid was replaced hourly for the total extraction time of 15 h. Aliquots of the extraction solutions were analysed without a concentration step by LC-MS.

The samples were separated by LC using an Acquity UPLC BMS system equipped with an Acquity CSH™ fluorophenyl column (1.7 µm, 2.1 × 75 mm) (all Waters, Manchester, UK). Methanol (A) and water (B) were used as the mobile phases and a gradient programme was applied: from 65% A to 100% A in 2.5 min, hold at 100% A for 1 min, from 100% A to 65% A in 0.1 min and hold at 65% A for 1 min. The flow rate was 0.5 ml min^{-1} and the column temperature was 40°C.

The column was coupled to the high-resolution MS Synapt G2 Si (Waters) with the following settings: ion-spray voltage 3.00 kV, source temperature 120°C, desolvation temperature 600°C, desolvation gas 600 l h^{-1}, nebuliser 6.5 bar, sampling cone 40, and a source offset of 80. Mass spectra were acquired in positive mode by electrospray ionisation and a TOF MS scan range of 50–1200 Da. Additionally to the mass spectra acquired at low collision energy (4 V), mass spectra acquired applying a collision energy ramp (10–40 V) were recorded. From those spectra information about the fragments of the molecules of interest can be deduced. For all measurements, leucine enkephalin was used as the lock mass. Accurate mass and fragmentation patterns were used for the identification of the oligomers.

Quantification was achieved by external calibration using the PET cyclic trimer of the first series as a standard for all analytes of interest since there are no standards available for the other oligomers. The calibration solutions were prepared in an equal mixture of acetonitrile and water and comprised six concentration steps in the range from 1 to 300 ng ml^{-1} (linear fit, R^2 = 0.998, LOD = 0.12 ng ml^{-1} (S/N = 3), LOQ = 0.40 ng ml^{-1} (S/N = 10)). The same MS response was assumed for all PET oligomers. Data were evaluated using the MassLynx™ MS software (Waters).

Determination of diffusion coefficients

The experimental diffusion coefficients were determined by plotting the oligomer concentrations of the individual migration solutions against the square root of time. From a linear correlation, the diffusion coefficient can be determined using:

$$\frac{m}{A} = 2c_{p,0}*\rho_P*\sqrt{\frac{D_P*t}{\pi}} \qquad (1)$$

where m/A is the area-related mass transfer of the oligomer into 50% ethanol (µg cm^{-2}); $c_{P,0}$ is the initial concentration of the oligomer in the polymer (µg g^{-1}); ρ_P is the density of the polymer material (g cm^{-3}); D_P is the diffusion coefficient (cm^2 s^{-1}); and t is the contact time (s). Due to the total immersion of the PET strips, the total active surface area of the sample was calculated to be 51.50 cm^2. Reordering equation (1):

$$M = 2c_{p,0}*\rho_P*\sqrt{\frac{D_P}{\pi}} \qquad (2)$$

where M is the slope of the trend line of the linear correlation between the mass transfer per contact area and the square root of time (μg s$^{-0.5}$ cm^{-2}), which allows one to calculate the diffusion coefficient using the slope of the respective graph.

The diffusion coefficients were also calculated based on the migration model of Piringer (Begley et al. 2005) using AKTS SML v4.51 software (Advanced Kinetics and Technology Solutions AG, Siders, Switzerland). Furthermore, the diffusion coefficient was calculated using the approach described by Welle (2013), which is based on the molecular volume of the substances. To that end equation (3) was used:

$$D_p = b*\frac{V^{\frac{a-\frac{1}{T}}{d}}}{c} \qquad (3)$$

where D_p is the diffusion coefficient (cm^2 s^{-1}); V is the molecular volume calculated using the free internet program molinspiration (http://www.molinspiration.com/cgi-bin/properties; accessed 17 October 2016); T is the temperature (K); and a, b, c and d are experimentally determined specific parameters for the prediction of the diffusion coefficient in PET: $a = 1.93*10^{-3}$ K^{-1}; $b = 2.37*10^{-6}$ cm^2 s^{-1}; $c = 11.1$ Å^3; and $d = 1.50*10^{-4}$ K^{-1}. The parameters resulted from the correlations of the activation energy with the molecular volume, the activation energy with the pre-exponential factor D_0 (in the Arrhenius approach) and the diffusion coefficient with the molecular volume (Welle 2013).

Results and discussion

PET bottle material was extracted to identify which oligomers were present and to determine their total concentrations in the polymer. We identified 11 cyclic PET oligomers in the extracts and assigned their probable structures via their accurate masses, isotope patterns and fragmentation patterns that correspond to the identification confidence level 2b, as described by Schymanski et al. (2014). The first-series cyclic trimer was confirmed by the measurement of a reference standard and, hence, identified at confidence level 1.

Five of the oligomers were found to represent the first series of oligomers that comprise an equal number of terephthalic acid and ethylene glycol units. Four were found to represent the second series in which one monoethylene glycol unit is replaced by a diethylene glycol unit. Finally, two oligomers were identified in which two monoethylene glycol units are replaced by diethylene glycol units, representing the third series of oligomers. Exemplarily, the chemical structure and fragmentation spectrum for one oligomer of each series is shown in Figure 1. Fragmentation spectra of the other oligomers are analogous. The common repetitive-mass loss from the molecular ion is 44 Da, which represents the loss of C_2H_4O. In the lower half of the mass range the fragmentation spectra of the oligomers show
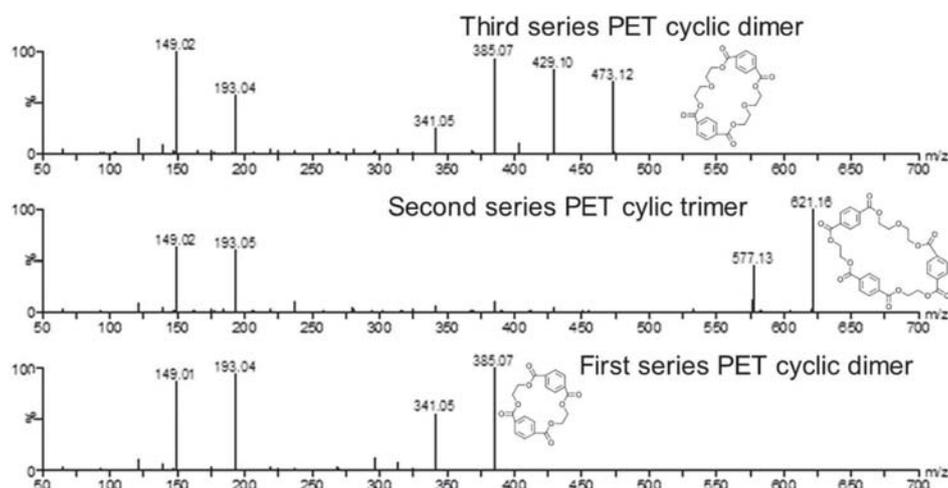
Figure 1. Chemical structures for cyclic PET oligomers and fragmentation spectra, one example for each series.

Table 1. Content ($c_{P,0}$) of cyclic oligomers in the investigated PET material.

Oligomer	$c_{P,0}$ (µg g^{-1})
First-series PET dimer	34
First-series PET trimer	2922
First-series PET tetramer	749
First-series PET pentamer	303
First-series PET hexamer	155
Second-series PET dimer	281
Second-series PET Trimer	157
Second-series PET tetramer	124
Second-series PET pentamer	84
Third-series PET dimer	65
Third-series PET trimer	11

intersections (149, 193 and 341 m/z), which confirm the similarity of their structures.

The concentrations $c_{P,0}$ of the PET oligomers in the bottle material are summarised in Table 1. A second extraction on the same specimen was conducted to check for completeness of the first extraction. In this post-extraction no more oligomers were detected. We calculated a total oligomer content of 0.5% in our PET material, which was slightly lower than the 0.6–1.3% reported in earlier investigations (Holland & Hay 2002; Lim et al. 2003). This may reflect technical improvements of the polymerisation process or the cleaning procedures applied to each polymer material, or it may be due to batch-to-batch or procedure-to-procedure variations, respectively. The first-series trimer was the most abundant oligomer, which is consistent with previous publications (Besnoin & Choi 1989; Holland & Hay 2002; Kim & Lee 2012a).

The diffusion coefficients of the oligomers in PET were determined using a kinetic migration experiment employing the food simulant 50% ethanol at 80°C. In other studies, 50% ethanol as a food simulant was shown to overestimate slightly the migrations compared with beverages (Franz & Welle 2008). The overestimation was explained by the swelling ability of ethanol regarding PET, especially at elevated temperatures (Franz et al. 2016). Therefore, in general testing with a simulant, which represents to a reasonable extent a worse-case scenario, is preferable and recommended to achieve sufficiently protective conclusions for risk assessment. We chose these severe test conditions since the oligomers are not expected to show high migration rates due to their relatively high molecular weight and the low basic diffusivity in the PET polymer. With these conditions we expected to be able actually to determine the migration kinetics based on reliably measurable migrations that would allow a proper comparison with migration models.

PET bottle wall strips were immersed in 50% ethanol within a pressurised steel cell and exposed in the closed cell for up to 15 h at 80°C, representing severe test conditions. After every 1 h, the solvent in the cell was replaced by fresh simulant, and we carried out up to 15 migration cycles. All migration solutions were analysed separately by LC-MS. With the exception of the first-series hexamer, the second-series pentamer and the third-series trimer, all the oligomers identified in the extracts were detected in the first migration cycle solution. Furthermore, we also detected linear oligomers that resulted from the reaction between the cyclic oligomers and ethanol (Figure 2). These linear ethyl esters have been identified in the migration solutions of the first cycle for the first-series dimer and trimer as well as in the second-series dimer. Since the formation of such reaction products was suspected, the theoretical masses of these molecules where separately extracted from the LC-MS chromatograms. The linear reaction products of the oligomers and ethanol were assigned based on the accurate mass, isotope and fragmentation pattern resulting in the identification at a confidence level 2b, according to Schymanski et al. The concentration of these linear oligomers in the migration solutions decreased with every migration cycle, indicating that these linear oligomers were probably the result of the reaction of ethanol with cyclic oligomers present in the migration solution rather than stemming from the reaction of ethanol with the polymer structure. Since this could not be verified experimentally, the concentration of the linear oligomers was not added to the concentration of the respective cyclic oligomers. However, only the linear ethyl ester of the cyclic trimer could be quantified in all cycles. Adding these concentrations to the cyclic PET trimer the respective diffusion coefficient would not change by the order of magnitude.

Taking into account the surface of a 0.5 l PET bottle (with a height of 20 cm, a diameter of 6 cm and cylindrical shape resulting in a contact area of 433 cm^2), which is in contact with 0.5 ml beverage (approximately 0.5 kg), the total migration of all PET oligomers under the applied test conditions is 0.181 mg kg^{-1}.
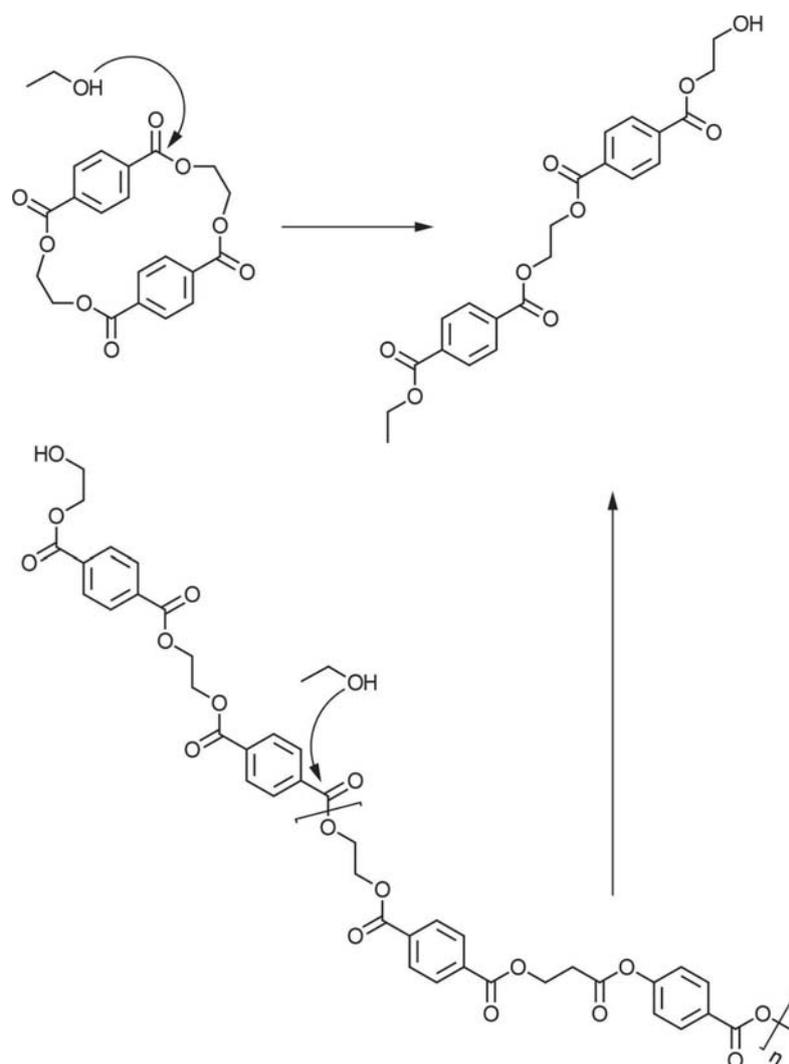
Figure 2. Reaction of the first-series cyclic PET dimer with ethanol or the polymer matrix resulting in ethanol with the linear first-series PET dimer ethyl ester.

The results of the migration kinetics are shown in Figure 3. The first-series cyclic trimer and the second-series cyclic dimer were detected up to the last of the 15 cycles with the cyclic first-series trimer as the most abundant oligomer in the migration solutions. The concentration of the other oligomers was below the LOQ (0.40 ng ml^{-1}) between the first and 10th cycles. We observed Fickian migration behaviour for the first-series timer and the second-series dimer, which was concluded from the fact that the square-root of time t versus the mass transfer per area showed a linear relationship. The diffusion coefficient was calculated from the slope of the line according to equation (2). The first- and third-series dimers and the second-series trimer showed Fickian behaviour in the early extraction cycles, but the low

migration rates that ended in values below the LOQ in the later migration cycles made it difficult to observe their behaviour in the later cycles. However, it can be assumed that the abovementioned oligomers continued to behave in a Fickian manner so that their diffusion coefficients could be determined from the early cycles, too.

The experimental diffusion coefficients thus derived are shown in Table 2. Note that the extrapolation of the trend lines to the y-axis leads for all oligomers to an intercept greater than zero for which an explanation is needed. Mechanistically, this means that there is already a certain concentration of the oligomers present in the food simulant immediately after the time point of immersion of the test specimen into the food simulant. This initial
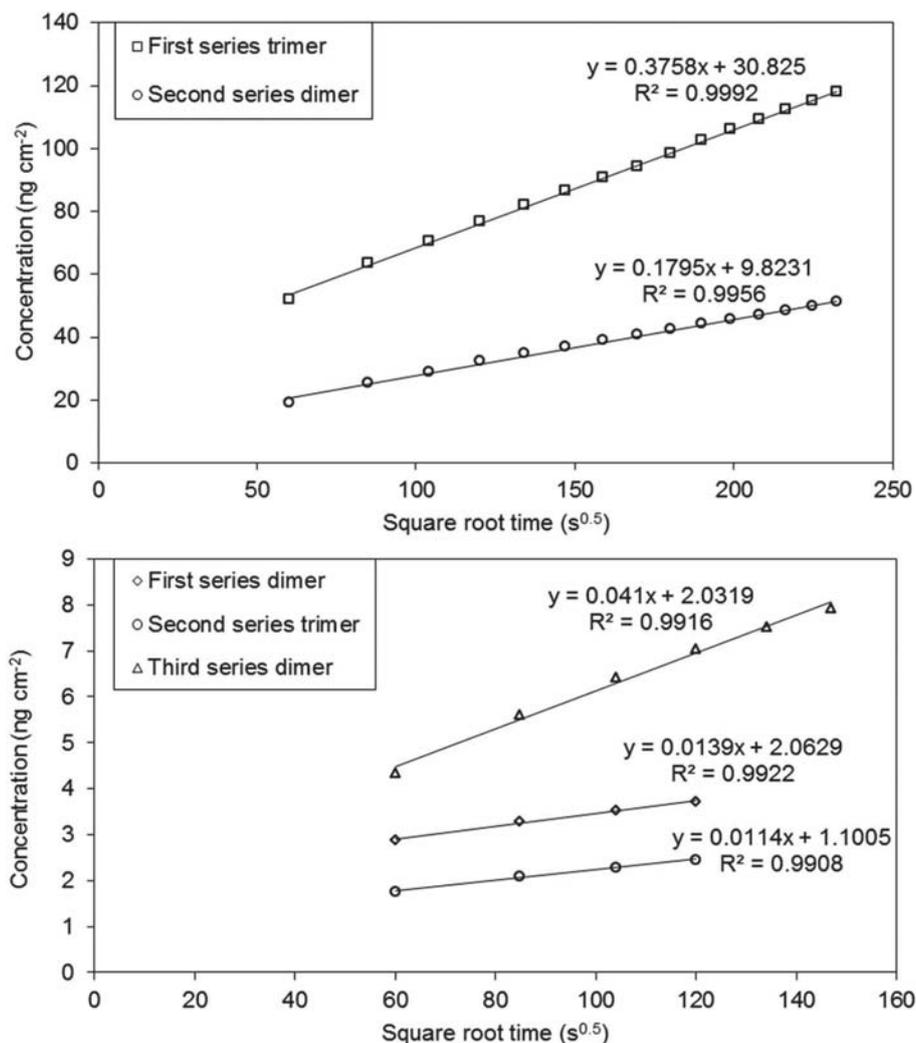
Figure 3. Migration of cyclic PET oligomers from a PET bottle into 50% ethanol at 80°C. The food simulant was replaced and analysed every hour for 15 cycles.

Table 2. Molecular weight, molecular volume (calculated using molinspiration), theoretical activation energy (calculated using the correlation between molecular volume and activation energy suggested by Welle: $(\ln (V/11.114))/0.0181 = E_A$), diffusion coefficients D (determined experimentally at 80°C, 50% ethanol), and D-values calculated using the approaches of Welle and Piringer of the PET oligomers (at 80°C).

	Molecular weight (g mol^{-1})	Molecular volume (Å^3)	Activation energy (kJ mol^{-1})	D experimental (cm^2 s^{-1})	D Welle approach (cm^2 s^{-1})	D Piringer approach (cm^2 s^{-1})
First-series cyclic oligomers						
Dimer	384.34	323.69	186	5.85*10^{-14}	3.71*10^{-15}	1.62*10^{-11}
Trimer	576.50	484.64	209	5.62*10^{-15}	1.57*10^{-16}	3.15*10^{-12}
Tetramer	768.67	645.59	224	–	2.81*10^{-17}	7.76*10^{-13}
Pentamer	960.84	806.54	237	–	7.37*10^{-18}	2.24*10^{-13}
Second-series cyclic oligomers						
Dimer	428.39	366.28	193	1.39*10^{-13}	8.47*10^{-16}	1.08*10^{-11}
Trimer	620.56	527.23	213	1.80*10^{-15}	9.49*10^{-17}	2.25*10^{-12}
Tetramer	812.73	688.18	228	–	1.91*10^{-17}	5.76*10^{-13}
Pentamer	1004.89	849.12	240	–	5.41*10^{-18}	1.72*10^{-13}
Third-series cyclic oligomers						
Dimer	472.44	408.87	199	1.35*10^{-13}	4.37*10^{-16}	7.37*10^{-12}

concentration in the food simulant at time $t = 0$ can be attributed to a certain mass of the oligomers on the surface of the material which is 'washed-off' with the first cycle. Such a phenomenon of oligomers assembled at the surface of a material is called blooming and has been observed by different

researchers (Ahjopalo et al. 2000; Schiraldi et al. 2001). It is attributed to a certain polarity incompatibility of oligomers with the host polymer matrix and the ability of the low molecular weight substances to diffuse to and concentrate on the surface of the PET material under the conditions of production. Due to the expectable low volatility of the oligomers, they will remain on the surface ready to be washed off rather than evaporate.

The observed Fickian behaviour of the PET oligomers has previously been reported for the major representative of the first-series cyclic PET oligomers, the cyclic trimer (Begley & Hollifield 1990a). Similar observations have not yet been reported for the other oligomers probably because of their low concentrations or low diffusion in the material resulting in low migration rates.

In a second step, the experimental diffusion coefficients were compared with the diffusion coefficients calculated using the diffusion modelling approaches by Piringer and Welle, respectively. The Piringer approach applies a fixed activation energy for a given polymer. For PET an activation energy of 100 kJ mol^{-1} is used as a default parameter for all possible migrants. A disadvantage related to PET is that for lower molecular weight substances (smaller than 80–90 Da) this approach tends to underestimate migration, and for higher molecular weight compounds it tends to overestimate the migration due to the fact that smaller substances have lower activation energies than the default value and larger molecules have higher or even much higher activation energies than 100 kJ mol^{-1}. For the PET oligomers we calculated activation energies of 186–240 kJ mol^{-1} based on the correlation between molecular volume and activation energy, as described by Welle (2013) (cf. Table 2), which is around twice the default activation energy set in the Piringer equation. Consequently, the calculated diffusion coefficients according to the Piringer equation are between one to three orders of magnitude higher than the experimentally determined ones. Based on these calculated diffusion coefficients, the migration of the PET oligomers would be heavily overestimated.

In 2013, Welle published a new approach to calculate the diffusion coefficient for potential migrants in PET polymer based on correlations between the activation energy and the molecular volume as key parameters for the diffusion of the migrants (Welle 2013). Using this approach, it was possible to derive a new equation (3) for the prediction of diffusion coefficients of migrants from PET using four polymer-specific parameters. Diffusion coefficients for the PET oligomers calculated with equation (3) are shown in Table 2. These were by one to three orders of magnitude lower than the experimental D-values obtained. This can be attributed to the swelling effect when ethanolic mixtures are in contact with PET, in particular under the applied high temperature condition. Widén et al. suggested that ethanol acts as a plasticiser and increases the mobility of the polymer chains leading to increased diffusion and, hence, higher migration rates (Widén et al. 2004). The ethanolic swelling effect has been observed and reported elsewhere (Franz & Welle 2008; Franz et al. 2016). It should be noted that the parameters of the approach used by Welle were derived under non-swelling conditions and, therefore, do not include diffusion accelerating effects caused by swelling due to increased uptake of food simulant into the polymer matrix. Another factor could be that the calculation of the molecular volumes for oligomers may be inaccurate and overestimate their volumes. Especially, the stacking of the planar aromatic rings could decrease the molecular volume. The experimental diffusion coefficients of the dimer of the second and third series show the highest deviations from the values calculated with the Welle approach. It may be possible that both dimers have a considerably smaller molecular volume than calculated and used in the Welle equation, which would result in higher diffusion coefficients. It should be noted that for the derivation of the polymer-specific parameters a, b, c and d, smaller molecules with a molecular weight up to 310 g mol^{-1} had been considered and that these structures did not have an ester function. Begley and Hollifield determined the diffusion coefficients of the PET cyclic trimer from crystallised PET (as it is used for microwave trays) into corn oil at 115, 146 and 176°C (Begley & Hollifield 1990a). Their D-values for the PET cyclic trimer were found to be $1.2*10^{-12}$ cm^2 s^{-1} at 115°C, $6.6*10^{-10}$ cm^2 s^{-1} at 149°C, and $2.9*10^{-9}$ cm^2 s^{-1} at 176°C. These values are in the same order of magnitude or one order of magnitude higher than the diffusion coefficients calculated by the Welle approach. This relativises the molecular volume

argument discussed above and qualifies more the ethanolic swelling effect as the major factor for the deviations.

Although the Welle equation shows a trend to underestimate slightly the diffusion coefficients and, hence, the migration potential of the PET oligomers, the diffusion coefficients calculated with the Welle approach fit better than the ones calculated with the Piringer equation (based on the default activation energy of 100 kJ mol^{-1}) with the experimentally determined values.

Conclusions

A migration study was conducted on PET material using 50% ethanol at 80°C as the food simulant in order to derive diffusion coefficients of PET oligomers under severe test conditions. These conditions were chosen to allow reliable measurements of migrations, but taking at the same time the swelling effects of ethanol on PET into account. The experimental determination of diffusion coefficients was possible for five oligomers including the first-series cyclic trimer which is the most abundant oligomer in PET. This is the first study to provide diffusion characteristics of oligomers other than the PET first-series cyclic trimer. Additionally, the diffusion coefficients were calculated using the models of Piringer and Welle. Taking into account the swelling effect of 50% ethanol on PET, the experimental diffusion coefficients support the applicability of the Welle model to PET oligomers. Therefore, the Welle equation might be a simple and fast way to calculate the migration of PET oligomers conveniently at very low migration levels, which otherwise would not be easily directly accessible by analytical means. In particular, for the first-series oligomers which are the major oligomers present and best measurable in migration solutions, the Piringer model (based on the PET-related default activation energy of 100 kJ mol^{-1}) shows large overestimation. Still, the migration into ethanolic food simulants, in particular at elevated temperatures, would be underestimated when applying the Welle equation. Therefore, when using the Welle equation for the prediction of oligomers into foods from PET, the type and nature of food should be carefully considered. As long as swelling effects due to the presence of ethanol can be excluded, the Welle equation appears to be applicable. If higher alcoholic drinks and spirits were the foods of concern,

then the diffusion coefficients from the Welle equation would underestimate the migration. Therefore, it seems to be worthwhile to study the migration of polyester oligomers into real foods experimentally and, further, explore the precise applicability of the Welle equation for migration evaluation of polyester oligomers in support of their risk assessment. This would not only be a PET-specific issue but also of general importance since the migration of polyester-related oligomers is a topic of increasing interest and relevance and should be considered more and more for compliance evaluation.

Disclosure statement

No potential conflict of interest was reported by the authors.

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