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Review

Identification and quantification of oligomers as potential migrants in plastics food contact materials with a focus in polycondensates – A review

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Abstract

Background: Over the last years the variety of food and beverage packaging has increased with the development of new plastic materials and (co)polymer modifications. Oligomers which are always present in polymers evoke attention as potential migrants, from a qualitatively and quantitatively viewpoint.

Scope and approach: This article deals with oligomers as potential migrants from plastics food contact materials and reviews their occurrence as well as analytical methods for their identification and quantification. Additionally a section about migration summarizes literature providing oligomer levels in food simulants and foods. Special attention was given to polycondensates since these represent a rapidly expanding polymer field due to increased numbers of (co)-monomers authorized by the EU.

Key findings and conclusions: Evaluating a polymer regarding the content and migration potential of its oligomers several factors like the separation of oligomers from the material, the choice of suitable separation and detection techniques for identification and quantification and the choice of an appropriate standard have to be considered. Generally, MS technologies coupled to liquid chromatography have been shown to represent the analytical approach of choice. This is, so far as the authors are aware of, the first review exclusively focusing on analytical methods for oligomers as polymer specific substances, which suggests to consider them as a separate polymer related and polymer type specific group besides the so-called non-intentionally added substances (NIAS).

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1. Introduction

The use of plastics steadily grows since they were discovered. In 2013 packaging applications represented the largest section of plastic uses in Europe (Plastic Europe, 2014). The mostly used polymers in this type of application are PE, PP, PET, PS and PVC. In the past the starting molecules for plastics have been mostly petrochemically based. However, today alternative plastic monomer units are searched for which can be produced from renewable sources like plants. Also, for environmental protection reasons biodegradability is taken into account in the development of new polymeric packaging materials.

During the last five decades the variety of food and beverage packagings increased with the development of new plastics materials and (co)polymer modifications. An inherent consequence is that oligomers which are always present in polymers gain increased attention as potential migrants not only from a quantitative but also from a qualitative aspect. An increasing number of new co-monomers will automatically raise the number of possible compositional oligomer structures.

Many requirements are put on polymeric food contact materials (FCM), for example physical protection of the groceries from temperature, compression and mechanical shock as well as barrier protection from oxygen, water vapor and dust. In addition the plastic FCM should prevent the product from bacterial contamination, viruses, mold and fungi and thus guarantee prolonged quality and safety. On the other side the food contact material might interact with the product. One of the processes occurring is migration, the transfer of molecules present in the FCM into the food. The migration of substances should not exceed unacceptable...
amounts because they may then pose a risk to the consumer. The European regulation on plastic materials intended to come into contact with food, Regulation 10/2011/EU, established specific rules for plastic materials and articles to be applied for their safe use (EU, 2011). A positive list is provided authorizing monomers, other starting substances and additives which can be used for the manufacturing process. Those substances are called intentionally added substances. Their specific or generic migration limits are listed in the Annex I of the regulation 10/2011/EU. Substances emerging through degradation of the polymeric material or additives and impurities of the starting materials are non-intentionally added and not listed in the authorization since it is impractical or even impossible to identify all impurities. These substances are generally called NIAS (non-intentionally added substances). For non-authorized substances their migration should not exceed a level of 0.01 mg/kg food. This, however, excludes substances that are carcinogenic, mutagenic or repertoxic (CMR substances). Particular attention is hereby paid to compounds with molecular weights up to 1000 Da. Substances with a higher molecular weight are generally regarded as physiologically not absorbable due to their size. For the detection and identification of NIAS untargeted screening approaches have been proposed (Nerin, Alfaro, Aznar, & Domeño, 2013). However, quantification of NIAS is difficult due to the many existing chemical classes of substances and their different analytical detectabilities and response factors. Today, the identification of unknown compounds is generally accomplished with high resolution mass spectrometry (HRMS). This provides the exact mass of a substance up to four decimal places which is essential for compound identification. Current MS software programs can calculate possible chemical formulas for the measured mass making use of the isotope patterns that are recorded by the instrument. Possible chemical structures can be suggested with the help of fragmentation experiments, knowledge of the sample and database searches like in Chemspider (www.chemspider.com) or the Norman Mass Bank (massbank.ufz.de).

Oligomers are often subsumed under the group of non-intentionally added substances when referring to components present in food contact materials (Nerin et al., 2013). However, oligomers are unavoidably formed during the polymerization process and could therefore be regarded as polymer specific accompanying substances. In fact, oligomer patterns formed are related to the polymerization process and can give information about a polymer type. They are not specifically regulated in the Regulation 10/2011/EU and are, in practical terms, therefore located in a legal ‘grey area’. The permanent extension of the EU positive list with new co-monomers as a consequence of industrial developments gives principally rise to an exponentially growing amount of new oligomers which might be present in food contact polymers as potential migrants. Usually the identity and biological properties or toxicological profiles of oligomers are not fully known. The same holds true concerning their migration rates into and exposure from packed foods. Traditionally, little toxicity testing has been conducted on oligomers and often safety assessment was based on toxicity data on the monomeric units, for instances under the assumption of complete hydrolysis of oligomers (Nelson, Patton, Arvidson, Lee, & Twaroski, 2011). However, in general not enough is known about oligomer degradation in the gastrointestinal system and therefore it might be necessary to evaluate the oligomeric structures separately as individual compounds or study their hydrolysis.

Prior to analysis the oligomers have to be extracted by an appropriate solvent from the polymer matrix. Additionally separation of the compounds present in the sample is essential for proper identification and quantification. This usually is accomplished by online gas or liquid chromatography. Oligomers have the advantage that they are related to their host polymer and therefore the monomeric unit(s) is (are) in general known. Hence masses for theoretical oligomers can be calculated and directly searched for in a mass spectrum which simplifies the identification by mass spectrometry. For the quantification of oligomers MS or other detection methods than or in combination with MS can be used, for example ultraviolet (UV), flame ionization (FI), evaporating light scattering (ELS), chemiluminescence nitrogen (CLN) and charged aerosol (CA). The problem hereby is the different response of compounds in the analytical detectors. Especially for mass spectrometric detection the response can vary strongly between molecules with different structural features. Often same response factors for a group of homologue oligomers are assumed. But this should, if possible, be verified for example with a quantitative response detection method like UV.

To study the oligomers in detail it is important to know of which monomers the respective polymer is composed. Main analytical questions and challenges are: How to identify oligomers present in food contact materials? How to quantify the amounts of oligomers migrating into food and beverages? How should risk assessment be conducted? The objective of this review is to summarize the relevant literature and by doing so to provide some answers to those questions based on the current state of published scientific knowledge. This review will focus more on polycondensation polymers which have been increasingly used and proposed as new alternative food contact materials rather than on polyhydrocarbons such as polyolefins formed by polyaddition. These more polar and partly biodegradable polymers contain high chemical diversity of oligomers which are analytically accessible by employment of modern LC-MS techniques.

2. Oligomers – definition, chemical formation, sources and species

Oligomers (oligo = a few - mers = parts) are defined as molecules consisting of a few monomer units. They usually contain between two and 40 repeating units depending on the chemical composition of the building block. Generally, species with a molecular weight below 1000 Da are considered as relevant potential migrants (EU, 2014). The toxicological interest is focused on these substances because only these molecules are supposed to be absorbed in the gastrointestinal tract (Donovan, Flynn, & Amidon, 1990). In reality the 1000 Da criterion is not a clear cut upper limit for absorption in the gastrointestinal tract. It was shown that absorption depends on several factors like the absorption pathway, molecular weight, polarity and shape of the absorbed molecule or region of the gastrointestinal tract (Bjarnason, Macpherson, & Hollander, 1995; Parlesak, Bode, & Bode, 1994). Schaefer et al. reported that 76–82% of the substances migrating into unpolar food simulants have a molecular weight <1000 Da and that substances migrating into polar food simulants have almost all a molecular weight <1000 Da (Schaefer, Mass, Simat & Steinhart, 2004). Generally, small molecules have higher diffusion rates and therefore a higher migration potential.

Chemical formation of oligomers occurs during the polymerization process either by incomplete polymerization or thermal or hydrolytic degradation of polymer chains during (re)processing of the polymeric material and conditions of use. The resulting oligomer pattern can be very complex and may consist of linear, branched and cyclic species which may have different migration properties and toxicological profiles (Schaefer, Ohm, & Simat, 2004).

Polymers are manufactured in different ways depending on the type of polymer and the underlying chemistry. Polyolefins are made of alkenes which polymerize under high pressure, high
temperature and in the presence of a catalyst to the respective polymer. This reaction is called chain-growth polymerization and proceeds via a radical mechanism. Polymers and polyamides are built in a polycondensation reaction or ring-opening polymerization with the loss of water. As starting material the corresponding monomers are used which react with the aid of catalysts to increasing polymer chains. The starting substances have to contain an acid group and an alcohol or amine group. Either one monomer contains both chemical groups in one molecule and reacts with itself or two components react with each other where one contains two alcohol/amine and the other two acid groups. For the ring-opening polymerization process small cyclic oligomers are used as starting materials. During those processes it can occur that short chains do not react further and stay in the polymer as oligomers. They can be trapped in a zigzag polymer chain so that the catalyst is not able to get in contact with the molecule any more. Through intramolecular reactions cyclic oligomers can be build which afterwards are unable to react further to a long polymer chain.

Other pathways of oligomer formation are degradation of the polymer either by thermal or irradiation energy. This may happen during sterilization treatments of packed foods with gamma or beta irradiation, high pressure, UV-light or ozone (Guillard, Mauricio-Iglesias, & Gontard, 2010). Degradation can also take place during transport or the storage phase through thermo-mechanical processes or through photolysis or photo oxidation induced by sunlight. Polycondensates can be hydrolyzed over the time when they are in contact with water or other solvents containing hydroxyl groups (Bor, Alin, & Hakkarainen, 2012). Oligomers from polyester or polyamides can be formed by different chemical reactions (Fig. 1). An intramolecular attack of a hydroxyl group of the polymer chain end can form a cyclic oligomer by a transesterification reaction. Intermolecular transesterifications of two short polymer molecules can cause linear low molecular mass oligomers. Further oligomer forming mechanisms are hydrolysis and thermally induced elimination reactions. Each of these mechanisms might not produce high amounts of oligomers by itself but they can sum up to significant concentrations in the polymer.

Due to the high number of monomers used for polymer production which is steadily increasing and the numerous decomposing processes a high variability of possible oligomers present in plastics FCM can emerge. Additionally the number and diversity of oligomers present in one material is increasing with polymer blending, grafting and cross-linking. This leads to an increased qualitative migration potential for oligomers from food contact plastics and makes the investigation of their presence, migration potential and toxicological effects more important.

An overview of possible monomers is shown in Table 1. The usual nomenclature for oligomers is as follows: if the oligomer consists of one sort of monomer unit the naming is consecutive monomer, dimer, trimer etc. for instance polyactic acid with the monomer lactic acid. If the oligomer consists of more than one type of monomer unit as in the example of polyethylene terephthalate a monomer comprises the two monomer units (dialcohol and dicarboxylic acid), a dimer contains two of each monomer units, a trimer three of each monomer units.

2.1. Polymers containing heteroatoms

Polyethylene terephthalate (PET) is a polyester composed of the monomers terephthalic acid and ethylene glycol. Typical examples of applications of PET are beverage bottles, flexible films, microwave containers and ovenable trays for frozen foods. The identity of
The migration of PEF oligomers with a molecular weight less than 1000 Da was recently evaluated by EFSA with the conclusion that their migration should not exceed 50 μg/kg food (EFSA, 2014b). The underlying monomers are ethylene glycol and 2,5-furandicarboxylic acid both of which can be produced from plants (e.g. sugar cane) (Eerhart, Faaij, & Patel, 2012).

Another new copolyester which is intended to partially replace PET consists of terephthalic acid and spiroglycol. For this polymer oligomer migration should not exceed 50 μg/kg food as well (EFSA, 2014a).

During the last years polylactic acid (PLA) has become one of the most attractive biopolymer materials for food packaging because it has material properties comparable with PET (Auras, Harte, & Selke, 2004). Food packaging applications include yoghurt cups and
water, milk and juice bottles. Oligomers present in PLA extracts can be cyclic or linear (Dopico-Garcia et al., 2013).

Polyamides, more precisely nylon, are frequently used for cooking utensils. There are different nylon materials nylon 6, nylon 6,6 and nylon 12 which vary in their monomers and way of production. Nylon 6 and nylon 12 are produced by ring-opening polymerization from the cyclic monomers caprolactam and laur-lactam, respectively. The numbers 6 and 12 reflect the carbon atom number of the monomer unit. Nylon 6,6 has similar physical properties like nylon 6 but is produced by a polycondensation reaction of the monomers hexamethylenediamine and adipic acid. Nylon materials are heat resistant and used for boiling-in-the-bag, as roasting or microwave bags and kitchen utensils. Hence, the material is heated up by the consumer which accelerates migration of already present linear and cyclic oligomers or leads to formation of oligomers by the heating process. Cyclic oligomers were found to be the dominating oligomer species inside nylon materials. Cyclic dimer to nonamer of nylon 6 as well as cyclic monomer to tetramer of nylon 6,6 were detected after dissolution/precipitation of the respective materials (Heimrich, Bonsch, Nickl, & Simat, 2012).

Polycarbonate (PC) is produced by reacting carbonyl chloride with bisphenol A. Applications are reusable beverage containers, ovenable trays for frozen food and prepared meals, boil-in-bag packs and microwave cookware. Because of the recent discussion about the safety of its monomer bisphenol A, polycarbonate is found less and less on the food packaging market and is increasingly replaced by other polymers e.g. Tritan® and other (Onghena et al., 2014).

Tritan®, a relatively new copolyester, intended to be potential replacement material for PC baby bottles, consist of the monomer units dimethyl terephthalate, 1,4-cyclohexanedimethanol and 2,2,4,4-tetramethyl-1,3-cyclobutanediol and shows a low migration potential of monomers and additives (Gwart, et al., 2013). No information about the oligomers present in Tritan® is available yet.

Epoxy-based polyester resins based on bisphenol A and epichlorhydrin are often used to coat cans. These coatings might release bisphenol-A diglycidyl ether (BADGE), the linear and cyclic dimers of BADGE and linear BADGE oligomers up to n = 7 into the packed foods (Biedermann & Grob, 1998). With newly developed can coatings that avoid the use of bisphenol A the number of possible oligomers increases (Bradley et al., 2009).

Polycaprolactone is a biodegradable polyester based on petrochemicals that is used to blend starch based polymers or as plasticizer for PVC. The monomer is ε-caprolactone. After subjecting cross-linked polycaprolactone to hydrolysis linear oligomeric structures (n = 2–7) were detected (Högland, Hakkarainen, Kowalczuk, Adamus, & Albertsson, 2008).

Many packaging materials consist of multilayer films as a consequence of the required food protection functions. Such films are made up of different plastic layers that are bonded by an adhesive layer which in most cases is made of polyurethane. This polymer consists of diol and diisocyanate units reacting in a polyaddition reaction. Both linear and branched polyurethanes exist. Branched polyurethanes are cross-linked by, for example, triisocyanates. Polyurethane oligomers can be cyclic or linear and are formed during pyrolysis at 250–325 °C (Lattimer, Polce, & Wesdemiotis, 1998). Also cyclic oligoesters of the used dialcohols and dicarboxylic acids formed as by-products can be present in polyurethane adhesives (Athenstädt, Funfrocken, & Schmidt, 2012).

2.2. Hydrocarbon polymers

Polyolefins (POs) is the overarching term used for a broad class of hydrocarbon polymers. These are different types of polyethylene (PE) (low-density PE (LDPE), linear low-density PE (LLDPE), high-density PE (HDPE)) and polypropylene (PP) all of which consist in various modifications in dependency of the polymerization and manufacturing process. These polymers represent the polymer type most frequently used in food packaging and they are used for snack food packaging, candy-bar overwraps, beverage bottles, soup wrappers and many other applications. POs are produced from the monomers ethylene and propylene, respectively. The functional olefinic carbon—carbon bond of the monomer is hereby consumed to build new carbon—carbon bonds of the polymer chain. The toxicologically relevant functional group of the monomer is therefore not any longer present in the polymer or possible oligomers. In the case of propylene oligomers are possible to emerge due to newly formed stereocenters. Oligomers of PE and PP materials can be found in organic solvent extracts of the polymers or in migration solutions when using lipophilic simulants capable to dissolve unipolar organic compounds (Alnafouri & Franz, 1999; Coulier, Orbons, & Rijk, 2007).

Polystyrene (PS) is the product of the radical polymerization of styrene. The main areas of application are in containers for yogurt, cream, cottage cheese, ice-cream, fruit juice, meat trays, biscuit trays, egg cartons, different food and drink cups and boxes for fresh products. PS usually contains a number of oligomers from n = 2–4 out of which the major oligomers, the dimers and trimers were detected in migration experiments with polystyrene (Choi, Jitsunari, Asakawa, & Sun Lee, 2005). For each oligomer different isomeric forms were found, three for the dimer and five for the trimer.

3. Analytical methods

The analysis of potential migrants of food contact materials is very complex and challenging. Knowledge about the material composition and the manufacturing process is hereby favorable. With an in-depth study of the sample compounds, which are definitely present like monomers and additives, can be determined. Additionally possible compounds arising from side or degradation reactions can be verified. Usually it is difficult to obtain sufficient information about a given sample. There are many different steps involved in the manufacture of a polymeric food contact material starting from chemical synthesis of the polymer from monomers and additives used, down to converting, including printing, into final food contact applications. With the knowledge about the contaminants present target analysis of the polymers and migrates can be conducted for intentionally added substances. The analysis of non-intentionally added substances is more challenging. First the unknown substances need to be identified in the polymer or migrate and then an appropriate quantification method has to be developed. This procedure holds for oligomers.

As mentioned before, if the monomers from which a polymer is built are known, possible oligomers which might be present in a polymeric food contact material can be determined. This simplifies the searching for and identification of the oligomers. Calculated oligomer masses can be systematically searched for in recorded mass spectra and the substances can be identified via their masses. Using high resolution mass analyzers like quadrupole-time-of-flight (Q-TOF) or ion-trap-time-of-flight (IT-TOF) allows collecting full scan spectra with accurate mass measurements and resolutions between 10,000 and 50,000 FWHM (full width at half maximum). With hybrid-orbitrap technologies even resolutions of 200,000 and more FWHM can be reached.

Not information about the precursor mass, structural information can be obtained by recording mass spectra at increased collision energy. These fragmentation experiments can give indications for functional groups. But the exact structure can only be confirmed by NMR or comparison of retention time and
fragmentation behavior with standard substances. Often oligomers can have the same empirical formula but different structures. This can be attributed to different reasons:

- different structural isomers of the starting monomers
- formed diasteromers when using mixed enantiomeric monomer material
- oligomers composed from same monomers which are ordered in a different way.

All these structural isomers have the same mass and cannot be distinguished by MS. However their different behavior in chromatographic separation can give a hint that different molecules with the same mass are present in the sample.

Oligomers of hydrocarbonpolymers like polyolefins and polystyrene are mostly volatile and therefore they are analyzed by GC coupled to a FID or MSD (Biedermann-Brem, Kasprick, Sinat, & Grob, 2012; Coulier et al., 2007; Greenwood, 2006). As an advantage GC–MS libraries can be used for identification. Oligomers from polar polymers are being analyzed mainly with liquid chromatography coupled to an appropriate detector because they are usually non-volatile due to their high molecular weight and weak electrostatic interactions due to their functional groups. The present review is focused on the analyses of oligomers emerging from more polar polymers of the polycondensates type which represent an increased area of food contact materials applications.

3.1. Sample treatment and identification

Identification of unknown oligomers can be performed on the polymeric material itself, an extract of the polymer or in a food simulant which was in contact with the polymer. Since the concentration of the oligomers will be high in the polymer for identification purposes it is advisable to analyze the pure sample without any further preparation. This is additionally time-saving. The analyses of the polymer can be accomplished by direct MS analysis with atmospheric solids analysis probe (ASAP) (Smith, Cameron, & Mosely, 2012), direct analysis in real time (DART) (Bridoux & Machuron-Mandard, 2013), desorption electrospray ionization (DESI) (Friia, Legros, Tortajada, & Buchmann, 2012), matrix assistant laser desorption/ionization (MALDI) (Lattimer et al., 1998) or direct probe analysis with APCI (Whitson, Erdodi, Kennedy, Lattimer, & Wesdemiotis, 2008). Those ionization techniques can be directly used in combination with high resolution MS instruments and reveal low molecular mass oligomers. The polymer can also be dissolved in an appropriate solvent and the diluted polymer solution analyzed by ESI-MS as described by Hunt et al. (Hunt, Binns, & Sheil, 1995). Another way to obtain a high concentration of oligomers is complete dissolution of the polymer in an appropriate solvent and precipitation of the polymer afterwards. The oligomers will stay in solution and can be analyzed as for example for polycarbonate oligomers in a recent study of Bignardi et al. (Bignardi, Cavazza, Corradini, & Salvadeo, 2014). Oligomers can also be obtained by solvent extraction of the polymer (Jenke et al., 2005). Extraction and dissolution approaches are more time consuming than direct analyses of the polymer but have the advantage of eliminating the polymer matrix which could degrade during the analyses methods and lead to oligomers not originally present inside the material.

3.2. Separation

To evaluate the migration potential of the identified oligomers in a plastic material quantification methods comprising separation and detection are needed. Separation can be conducted via gas chromatography, liquid chromatography, gel permeation chromatography and capillary electrophoresis. Separation of oligomeric substances from polar polymers is more often accomplished with liquid-based separation techniques (HPLC, CE) than with gas chromatography. Reversed-phase liquid chromatography (RP-HPLC) is hereby the most widely used chromatographic separation system when investigating polymer oligomers. A chromatographic separation step before MS detection is recommended because other contaminants might have a similar molecular mass as the oligomers. It has to be taken into account that analytical artefacts from solvents and applied procedures can arise. Those have to be identified and disregarded from the oligomers present in polymer materials.

3.3. Detection and quantification

Mass spectrometry with atmospheric pressure ionization is nowadays the detection method of choice when analyzing polar polymers. These techniques have a wide range of application, are compatible with LC-flow rates and are robust in performance. Due to the availability of different ionization methods like electrospray (ESI), atmospheric pressure chemical (APCI) and atmospheric pressure photo ionization (APPI) as well as direct probe it is possible to ionize different types of compounds: polar, medium polar and non-polar migrants like additives, oligomers and their degradation products with a wide range of molecular weight, different polarity and thermal instability (Paine, Barker, & Blanksby, 2014; Rizzarelli & Carroccio, 2014). Since these methods are soft ionization methods in-source-fragmentation is seldom observed. However, it has to be considered that especially with the often used ESI adduct formation (H+-, Na+-, K+-, NH4+,-, CH3CHOH-) and doubly or multiply charged ions can occur (Jonkers, Govers, & De Voogt, 2005; Klun, Andreušek, & Krzan, 2001). This makes interpretation of mass spectra more complicated. Other detection methods like ultraviolet (UV), charged aerosol (CA), evaporative light scattering (ELS) and chemiluminescence nitrogen (CLN) are mostly used for confirmation or quantification purposes. Triple quadrupole detectors are frequently used mass analyzers for quantification purposes because they have a high sensitivity and selectivity.

The choice of an appropriate standard for calibration and determination of concentration levels is challenging due to varying response of different molecules to the most detection methods. Especially in the field of LC-MS the response depends strongly on the ionization availability of the chosen technique and the analyte of interest. Quantification methods can be divided into different approaches:

- using the monomer as external standard and if available before determined response factors
- using one oligomeric substance as external standard for all oligomers
- hydrolyze the oligomers to the monomer and determine the overall monomer content of all oligomers
- using a commercially available substance with structural features similar to the oligomers as external standard
- using, if available, for each separate oligomer the respective oligomer as external standard.

3.4. Examples how to identify oligomers

Nasser et al. identified the structure of PET cyclic oligomers by different nuclear resonance spectroscopic (NMR) experiments and ESI-MS (Nasser et al., 2005). They could verify that the cyclic trimer...
and tetramer obtained by dichloromethane extraction of PET bottles had 1,4-dissubstituted aromatic rings. The multiplicity of the hydrogen atoms of the cyclic dimer indicated instead 1,3-dissubstituted aromatic rings which is related to the presence of isophthalic acid in the PET production. Additionally the cyclic trimer with a diethylene glycol unit could be identified by NMR, MS and MS/MS. It was shown that the aromatic rings in this molecule are 1,4-dissubstituted, too.

Freire et al. studied the oligomer formation in ovenable PET samples under high temperature conditions (Freire, Damant, Castle, & Reyes, 1999). PET samples were heated at 150 °C, 260 °C and 270 °C for different times and the amount of all oligomers formed was determined by LC-APCI-MS. Cyclic oligomers without and with diethylene glycol unit as well as linear oligomers with diethylene glycol units were identified. The amount of cyclic oligomers did not change with increasing temperature or over longer time periods. Linear PET oligomers containing a diethylene glycol unit showed increased levels in PET samples heated at 260 °C and 270 °C, concluding that degradation of the material starts at 260 °C and that linear oligomers are the main degradation products.

The co-polyester Ecoflex is composed of terephthalic acid, adipic acid and 1,4-butandiole. The oligomers present in the original sample and in samples after partial alkaline degradation were identified and characterized by LC-ESI-MS (Song et al., 2011). This example shows the possible complexity of oligomers in a polymer sample made from three monomer units. In the positive ionization mode cyclic oligomers are detected as $[\text{M-Na}^+]^+$ between $m/z$ 350–2000 Da. These cyclic molecules are not observed in the negative ionization mode due to absence of an acidic proton. Linear oligomers are observed in the negative ($[\text{M-H}^-]^{-}$) and positive ionization mode ($[\text{M-Na}^+]^+$) in the mass range $m/z$ 326–1976 Da and 350–2000 Da, respectively. Cyclic oligomers had equal numbers of polyacids and butanediol units but with varying compositions of terephthalic and adipic acid which is expressed by a difference of $m/z$ 20 Da in the mass spectra for each changed unit. Linear oligomers had varying end group compositions. Structural confirmation was conducted with MS² experiments of the $^{13}$C isotope peaks. Retention time against mass plots of the obtained LC-MS data showed a complex elution pattern of the linear and cyclic oligomers.

Newly developed polyester resins for food can coatings are composed of different polyols and polyacids. Since the monomer units used are known the theoretically possible oligomers could be calculated. This was done by Bradley et al. with nine common polyols and three polyacids (Bradley et al., 2009). They obtained over 1000 possibilities for cyclic and linear oligomers of varying size and with varying combinations of the monomer units. With help of the built database and using HPLC-ESI-TOF-MS they could identify 13 oligomers, twelve of them with a cyclic structure, which covered a total of 28 isomeric forms in an acetonitrile extract of a metal panel coated with a polyester lacquer. The mass errors were less than 5 ppm for all structures. The analysis revealed that the polyester resin was based on one polyacid and five polyols.

### 3.5. Examples how to quantify oligomers

Mutsuga et al. developed a quantification method for the migrating oligomers from polyactic acid polymer (Mutsuga, Kawamura, & Tanamoto, 2008). They followed two tracks which were compared. First PLA oligomer levels present in test extracts were determined by using lactide as external standard for all oligomers. Additionally the extracts were subjected to alkali decomposition. The oligomers were hydrolyzed to the monomer lactic acid by adding sodium hydroxide to the migration solution. Quantification was conducted by using lactic acid as standard. The analysis was done with LC-ESI-MS. Linear PLA oligomers ($n = 3–13$) were found inside the migration solutions. The amount of lactic acid, lactide and oligomers determined by the alkali decomposition method was similar to the total amount of the migrating oligomers calculated using lactide as external standard for the oligomers. In all cases the quantities of the alkali decomposition were slightly higher than the total migration. This difference was explained by the notion that oligomers higher than the 13mer were present but below detection limit; some oligomers up to the 13mer were below the limit of quantification or that the different MS response of lactide and PLA oligomers led to an underestimation of oligomer levels. This publication is a good example how to do a non-time and material-consuming quantification using the monomeric unit as standard and simultaneously determining the oligomer pattern in the sample by using LC.

Another and more elaborate quantification method for linear PLA oligomers up to the nonamer based on calibration factors derived from lactic acid calibration (cyclic dimer) was published by Codari et al. (Codari, Moscatelli, Storti, & Morbidelli, 2010). Analysis and detection was carried out by RP-HPLC-UV (210 nm). The response factor of lactide was calculated by analyzing solutions of different concentrations. Calibration factors of the linear dimer and lactic acid were determined based on the hydrolysis reaction of lactide. Lactide was dissolved in water and during the reaction to initially the linear dimer and next to lactic acid the concentrations of these substances were monitored. Using the initial lactide concentration and the response factor of the resulting linear dimer and lactic acid, respectively, calibration factors of these substances for this HPLC-UV method were calculated. Higher PLA oligomers were isolated using semi-preparative HPLC, subjected to hydrolysis and the developing hydrolysis products monitored. The moles of the formed lactic acid and linear PLA dimer were used to estimate the consumed moles of the higher oligomers under investigation and the corresponding calibration factors were evaluated. A linear relation between the reciprocal of the calibration factors and the chain length was observed.

Mengerink et al. developed a separation and quantification method for linear and cyclic nylon 6 oligomers without any sample preparation by sandwich injection of the dissolved polymer into a HPLC system. They published a three parted study concerning this topic. The second part of this study describes the detection and quantification method (Mengerink et al., 2000). Cyclic oligomers were detected by low-wavelength UV (210 nm) and linear oligomers by fluorescence after selective post-column derivatization reaction. The equivalent group absorbance concept was applied for semi-quantitative analysis since the chromophores of the nylon oligomers are separated by methylene groups. UV-absorption coefficients of non-available higher cyclic oligomers were calculated and applied for concentration determination. For linear oligomers the calibration factors for 6-aminocaproic acid were calculated to determine their concentrations via fluorescence detection. To correct for different quantum yield additionally an empirical quench factor had to be calculated. The optimized HPLC-UV-fluorescent detection method by Mengerink et al. is suitable to determine the total content of each single oligomer inside a polyamide material. The quantification approach could also be used to determine oligomer levels in migrates.

A quantification method for cyclic nylon oligomers with HPLC-CLND was published by Heimrich and others (Heimrich et al., 2012). The chemiluminescence nitrogen detector (CLND) provides an equimolar nitrogen response to any nitrogen containing substance by converting organic matter into CO₂, H₂O and NO. Cyclic nylon oligomers were synthesized to prove the equimolar nitrogen response of the CLND and a quantification method was developed based on a single-substance calibration with caffeine. Additionally
UV response factors for the cyclic oligomers of nylon 6 (n = 2–9) and nylon 6,6 (n = 1–4) relative to caprolactam were calculated. Prior to the CLN detection the oligomers were identified by HPLC-ESI-T0F-MS in the positive ionization mode. Four different types of nylon granulates were investigated by dissolution/precipitation experiments: PA6 (monomer unit caprolactam), PAMX6 (m-xylylene diamine and adipic acid), PA6/66 (caprolactam, 1,6-diamino hexane and adipic acid) and PA6I/6T (1,6-diamino hexane, isophthalic acid and terephthalic acid). Cyclic oligomers of varying size were determined in amounts between 0.84% and 1.95% in different materials. Linear oligomers were not identified in any of the PA materials. An elaborated discussion about relative response factors determined via HPLC-UV-CLND regarding caprolactam of the cyclic oligomers of PA6 (up to n = 9) and PA6,6 (up to n = 3) determined in their own work and reported in literature can be found in the publication.

An analytical method for nylon 12 oligomers was developed by Stoffers et al. (Stoffers, Brandl, Franz & Linssen, 2003). The monomer, laurolactam, and the cyclic dimer, trimer and tetramer were separated by HPLC and detected by UV or MS. Both detection methods are sensitive enough to quantify the analytes below the specific migration limit of laurolactam. The authors succeeded in purifying these dimer and trimer with preparative HPLC which was used for response factor studies. Laurolactam related relative response factors for the oligomers were calculated for UV as well as MS detection by dividing the slopes of the respective calibration graphs (slope oligomer/slope laurolactam). UV response factors (207 nm) were 0.68 ± 0.01 for the cyclic dimer and 0.85 ± 0.02 for the cyclic trimer. Relative response factors for MS detection varied highly due to day to day variability of the mass spectrometer. For the dimer the response factor ranged from 1.2 to 1.4 and for the cyclic trimer from 2.7 to 3.2. With the established response factors both nylon 12 cyclic dimer and cyclic trimer can be quantified using the commercially accessible monomer laurolactam.

Oligomers present in ten different products made from PET material were identified by Kim and Lee using HPLC-ESI-MS (Kim & Lee, 2012b). They identified two different series of cyclic oligomers in polymer extracts made with dichloromethane. Oligomers of the first series were composed of terephthalic acid and monoethylene glycol, oligomers of the other series contained a diethylene glycol unit substituting a monoethylene glycol unit. The cyclic PET trimer was isolated in high amounts for structural analysis by NMR. This purified substance was later used as external standard for quantification of all detected oligomers with HPLC-UV. Cyclic oligomers from the dimer to the heptamer were identified by HPLC-ESI-MS. Higher molecular weight oligomers up to the undecamer were identified by Q-TOF-MS. Cyclic oligomers n = 2–11 of the second series of oligomers have been detected as well. Additionally linear oligomers from the dimer to the tetramer with a diethylene glycol unit were present in the extracts. The total oligomer content ranged from 0.40 to 1.16% of the sample weight with the cyclic trimer as most abundant oligomer with 42.5–67.6% of the total oligomer content. Furthermore extracts with 50% acetonitrile have been prepared which showed a different oligomer pattern. The fraction of the linear oligomers of the total oligomer content in the acetonitrile extract was about 50–80%. Cyclic oligomers with diethylene glycol units contributed 1–30% to the total oligomer and monomer content. Contrary to what was observed for the dichloromethane extract, the portion of the cyclic dimer and trimer of the total oligomer and monomer content was very low in the acetonitrile extract. Overall the total amount of oligomers extracted with 50% acetonitrile was around 35 times less than the amount of oligomers extracted with dichloromethane.

Schaefer et al. determined the amount of cyclic oligoesters migrating from polyester can coatings by the comparison of the response of three different detection methods (Schaefer, Ohm et al., 2004). They developed a concept for the identification and quantification of oligomeric migrants from polyesters composed of different monomer units. Additionally the polyester migrants were hydrolyzed to their monomers and analyzed by GC-FID and HPLC-UV-ESI-MS. The analysis of the hydrolysis products allowed compositional identification of the alcohol and acid monomers. The three detectors used for quantification were ELS, UV and MS. The molecular response of the ELSD depends on the molecular weight of the analytes and the molecular response of the UV detector depends on the amount of aromatic rings in the molecules of interest. With LC-MS nine different cyclic oligoesters which covered twenty isomers were identified to migrate out of the three polyester can coatings. Because of different UV/Response of the molecules due to different molecular weight-chromophore-ratio, the researchers used the chromophore concentration instead of the substance concentration for calibration. This method can be applied for aromatic oligoesters. The cyclic PET trimer was used as external calibrator for all identified oligomers. Another option for quantification was ELS detection. Amounts of oligomers determined with the two detection methods UV and ELS were compared directly. It was concluded that ELSD overestimates the amount of oligomers with a higher mass than the used external standard (cyclic PET trimer). This overestimation might be due to the fact that the higher molecular weight oligomers are less volatile than the cyclic trimer standard. Besides the UV determined levels might be underestimations. This can be put down to the fact that oligomers containing dialcohols which have a higher molecular weight than ethyleneglycol have a lower UV active content than oligomers with less aliphatic content.

4. Migration of oligomers

Migration is the term used to describe the mass transfer from food contact material into food by physical processes. For reproducibility and analytical reasons like possible ion suppression due to matrix interferences migration is tested using food simulants (EU, 2011). Furthermore testing conditions like time, temperature and test medium are standardized, too. A distinction is made between specific migration were only a single species or a chemical group of migrants is measured and overall migration which is intended to cover the sum of all migrating substances. In general migration obeys the second Fick’s law and is controlled by diffusion in polymer and food as well as by partitioning between them. An extensive introduction into theoretical and practical aspects of migration with numerous scientific and regulatory contributions is given in a monograph (Piringer & Baner, 2008). Another comprehensive publication describes how migration and exposure of contaminants can be mathematically predicted which saves time and costs for elaborated experiments when crucial input parameters for migration modeling are known or can be predicted (Franz, 2005).

In the EU Regulation 10/2011/EU on plastic materials intended to come into contact with food oligomers are not specifically regulated (EU, 2011). Therefore, in the past, it was assumed their migration restriction is covered by the overall migration limit which is 10 mg of total constituents released per dm² food contact surface. This situation is paralleled by the fact that national regulations of oligomers have not been established in Europe and explains why studies dealing with their migration into foods and exposure via food consumption are very rare. However, during recent years oligomers were considered more and more as relevant potential migrants of interest from polymeric FCM. A reason for that can be seen in a lack of knowledge about their physiological degradation such as hydrolysis into the underlying monomers. As a
Oligomer migration from oven or microwave usable food contact polymers like nylon and PET was investigated by different research groups. The presence of low molecular weight oligomers in PET is well known. It was shown that 29% of the available PET oligomers can migrate from a PET/paperboard tray heated at 176°C for 30 min into the food simulant oil (Begley, Gay, & Hollifield, 1995). Begley and Hollifield determined the migration of cyclic PET oligomers from ovenable and microwavable trays at high temperatures into corn oil (Begley & Hollifield, 1990). Migrates were analyzed by HPLC-UV and PET cyclic trimer was used as external standard for all detected oligomers (n = 3−8). Samples were exposed to corn oil for 3 min in a 577-W microwave oven. Migration levels of cyclic trimer, tetrramer, pentamer, hexamer, heptamer and octamer from one of the investigated trays were 0.0078 mg/dm², 0.0012 mg/dm², 7.0*10⁻⁴ mg/dm², 4.5*10⁻⁴ mg/dm², 2.2*10⁻⁴ mg/cm² and 1.4*10⁻⁴ mg/cm², respectively, which makes a total of 0.01 mg/dm². A similar result was found for another PET microwave susceptor board where 0.0078 mg/dm² of PET oligomers (n = 3−6) migrated into corn oil after 3 min at 644 W (Begley, Davidson, & Hollifield, 1996). Jickells et al. determined the migration of oligomers into corn oil from crystalline PET trays after microwave treatment as 0.14 mg/dm² (Jickells, Gramshaw, Castle, & Gilbert, 1992). The higher value can arise from the previous microwave treatment of the material for 12 h at 220 W and the time and temperature of the migration experiment (1 h/121°C). Castle et al. measured PET oligomer migration values of 1.4−4.2 mg/dm² into olive oil after 2 h/175°C for four different PET trays (Castle, Mayo, Crews, & Gilbert, 1989). They also determined PET oligomer migration levels from PET trays or roasting bags into fatty foods like lasagna, sausages, French fries, pizza and fruit as watery foods under different heating conditions. Migration values ranged from 0.02 to 2.73 mg/kg for fatty foods and for fruits from 0.10 to 0.21 mg/kg. PET oligomer migration into beverages was found to be between <0.05 and 0.29 mg/kg. Migration values into microwaveable foods were also determined by Begley et al. (Begley et al., 1990). Foods were prepared at 644 W for 1.75−4.5 min and migrating oligomers (n = 3−5) reached concentrations between 0.169 and 6.57 mg/kg for popcorn, pizza, French fries, fish sticks and waffles.

Migration of PET oligomers from roasting bags into olive oil was reported by López-Cervantes and co-workers (López-Cervantes, Sánchez-Machado, Simal-Lozano, & Paseiro-Losada, 2003). Oligomers from the dimer to the pentamer were identified with MS and quantification was done by HPLC-UV using the cyclic trimer as external standard for all oligomers. Total oligomer content was found to make up 4% (by weight) of the polymer. Migration testing into olive oil was conducted for 7 min at 850 W in a microwave oven and for 60 min at 200°C in a conventional oven. From two roasting bags tested one showed the same migration level of PET oligomers (n = 2−5) for microwave and conventional oven heating (2.73 ± 0.06 mg/dm² and 2.72 ± 0.05 mg/dm², respectively) and the other one had different migration levels for the different testing conditions: 4.09 ± 0.09 mg/dm² for oligomer migration at microwave heating and 3.51 ± 0.06 mg/dm² for conventional heating.

Specific migration of PET oligomers from PET food containers into non-fatty food simulants was determined as a comparison between official EU and Asian test regimes by Kim and Lee (Kim & Lee, 2012a). They compared EU versus Asian test conditions and measured oligomer migration levels in the food simulants by HPLC-UV. Six PET bottles and three PET trays were tested as follows: distilled water 60°C/0.5 h (Korea/Japan); 40°C/10 d (EU); 4% acetic acid 60°C/5 h (Korea/Japan); 3% acetic acid 40°C/10 d (EU); 20% ethanol 60°C/0.5 h (Korea/Japan); 10% ethanol 40°C/10 d (EU); n-Heptane 25°C/1 h (Korea/Japan); iso-octane 20°C/48 h (EU) and 95% ethanol 40°C/10 d (EU). Quantified oligomers included the linear PET dimer and trimer with one diethylene glycol glycol unit, the cyclic dimer and trimer as well as the cyclic dimer and trimer with one diethylene glycol unit. Specific migration levels of PET oligomers were higher from trays than from bottles which is possibly due to lower crystallinity of the trays. It was shown that migration of oligomers and monomers into the food simulant 95% ethanol, with 0.00536 mg/dm² for bottles and 0.042 mg/dm² for trays, was significantly higher than into other simulants. They suggested that 95% ethanol migration stimulant is exaggerating the migration rate. Ethanol might be unsuitable as an alternative fatty food simulants and other non-polar solvents should be used instead. The total migration values of oligomers and monomers for all other food simulants and test conditions were in the range of 0.05*10⁻³−0.00246 mg/dm². The conclusion was that EU test conditions tend to give higher results for non-fatty food simulants than Asian test conditions.

Soto-Valdez et al. (Soto-Valdez, Gramshaw, & Vandenburg, 1997) identified and quantified nylon oligomers from nylon microwave and roasting bags with a thickness of 18.1 ± 0.64 μm. Identification was performed by analyzing a methanolic extract of the plastic with HPLC-UV and offline FAB (fast atom bombardment). Cyclic nylon 6,6 oligomers up to the tetramer and cyclic nylon 6 oligomers up to the octamer were identified. Migration of those oligomers and monomers into olive oil revealed 0.916 mg/dm² which is 41.8% of the total oligomer content present in the material. This value supports the findings from Begley et al. (Begley et al., 1995) who investigated a similar baking bag (thickness 25 μm). For quantification caprolactam and the response factor of Barkby (Barkby & Lawson, 1993) were used. Chicken prepared in microwave and roasting bags from nylon have been analyzed for nylon 6,6 monomer, dimer and trimer and nylon 6 monomer (Gramshaw & Soto-Valdez, 1998). Chicken skin, juices and meat were studied separately. Analysis was done with LC-MS and quantification with an internal 2-azacyclononane standard. Juices and skin were found to be more contaminated with nylon monomers and oligomers since in these cases there was direct contact to the roasting bags. For the whole chicken levels of nylon 6,6 monomer and nylon 6 dimer were found to be 3.86 μg/g, for the nylon 6,6 dimer 2.18 μg/g and non-detectable for the nylon 6,6 trimer. The trimer levels for juice and skin ranged between <1.1−6.6 μg/g and <1.1−7.6 μg/g, respectively.

Begley et al. investigated migration of nylon oligomers out of commercial oven roasting nylon 6/6,6 bags with a thickness of 25 μm (Begley et al., 1995). Residual oligomers in the polymer were determined via a dissolution/precipitation procedure. Oligomers were identified by HPLC-MS and quantified with HPLC-UV using caprolactam as external standard. Nylon 6 oligomers from dimer to heptamer and nylon 6,6 oligomers from monomer to tetramer gave a total oligomer content of 10.5 mg/g polymer. Migration experiments from these oven baking bags into oil at 176°C for 30 min revealed that 43% of oligomers present in the polymer migrated into the food simulant which equates to a migration of 15.5 mg/g and 80 μm were boiled in water for 1−6 h. The migration of cyclic oligomers up to the nonamer was confirmed by LC-MS. Quantification was carried out using LC-UV with caprolactam as external standard under usage of the individual response factors for each oligomer regarding caprolactam as external standard determined by Bonifaci et al. and Sedgwick (private communication). After 1 h of boiling the films released around 1% of weight into the water. The amount of total migrating oligomers (n = 1−8)
was 2.4 mg/dm² for the 15 μm film and 8.5 mg/dm² for the 80 μm film. Trimer, tetramer, pentamer and hexamer showed higher migration levels than the dimer.

Stoffers et al. investigated different food simulants for the migration of nylon 12 monomer and oligomers from three nylon 12 films with the objective to search for a suitable alternative fatty food simulant in contact with nylon 12 (Stoffers, Dekker, Linsen, Störmer, & Franz, 2003). Migration of the monomer (laurolactam) and low molecular weight oligomers into isooctane, 95% ethanol, 50% ethanol and water was tested and compared with the results obtained for olive oil. Measured migration values into olive oil after 2 h at 100 °C were 0.4–0.6, 0.3–0.6 and 0.1 mg/dm² for the monomer, dimer and trimer, respectively. 95% ethanol was found to significantly overestimate the olive oil results whereas iso-octane did underestimate them. Water was found to be the best alternative to simulate the monomer migration into olive oil, whereas migration of the dimer into water was at the detection limit (not specified) and migration of the trimer into water was not detected. This can be explained by the limited solubility of the oligomers in water. However, 50% ethanol was slightly overestimating the olive oil values for the dimer and trimer. No general statement for all migrants was made regarding the best food simulant alternative to fat. This study shows that it is challenging and almost impossible to find a suitable food simulant which depicts the migration of all substances of interest. Similar results at 100 °C for 2 h were found for nylon 6 and nylon 6.6 by Heimrich and coworkers (Heimrich, Nickl, Bönisch, & Simat, 2015). Isooctane underestimated the migration of cyclic oligomers into olive oil and ethanolic and aqueous food simulants shown to be worst case for cyclic oligomer migration.

Migration of linear oligomers from PLA into different food simulants was studied by Mutsuga et al. (Mutsuga et al., 2008) using the quantification method as described above. They subjected four different PLA sheets to contact with water, 4% acetic acid and using the quantification method was studied by Mutsuga et al. (Mutsuga et al., 2008) cyclic oligomer migration. Ethanol and aqueous food simulants shown to be worst case for underestimated the migration of cyclic oligomers into olive oil and impossible to determine oligomer levels were 0.02 mg/dm² and 0.116 mg/dm², respectively. Additionally the effect of temperature and time on the oligomer migration was studied. Oligomer migration into water was observed under conditions of 95 °C for 30 min. Under these conditions PLA oligomers were only detected into 20% ethanol and determined oligomer levels were 0.02 mg/dm² and 0.116 mg/dm², respectively. Additionally the effect of temperature and time on the oligomer migration was studied. Oligomer migration into water was observed under conditions of 95 °C for 30 min or after 6 months at 40 °C. Interestingly, when the test temperature was 60 °C oligomer migration into water took place already after 1 day for one PLA sample and for three other samples after 5 days from which it was concluded that temperatures around 60 °C may cause PLA hydrolysis. It was also noted that PLA materials with higher o-lactic acid content may decompose faster.

Choi et al. studied the time-dependent migration of styrene oligomers from PS into water and heptane at different temperatures. Derived from these data they calculated the diffusion coefficients in the polymer and activation energies for the migrants (Choi et al., 2005). Residual levels of styrene dimers and trimers in several PS food packaging articles and disposable food contact articles (n = 24) were shown to range between 130–2900 mg/kg for the dimer and 220–16000 mg/kg for the trimer (Genuadi, Nyman, & Begley, 2014). Also diffusion and partitioning coefficients for eight PS materials (five HIPS, one XPS, one EPS, one GPPS) for three food simulants (10% ethanol, 50% ethanol, 95% ethanol) were determined. The results obtained indicate that migration of styrene dimers and trimers into food simulants is very low and largely partition-limited as indicated by the high calculated partitioning coefficients. This was confirmed by the low concentrations of styrene dimers and trimers measured in food (<5 mg/g).

| Table 2 | summarizes migration values of some selected publications. With the exception of nylon 6 films the overall migration values of oligomers are far below the limit of 10 mg/dm² for all investigated materials. The reason for the high values for nylon 6 can be seen in severe swelling effects with water at the high test temperature (100 °C).

5. Polymeric additives

Several additives are used to obtain plastic materials which are more convenient for practical application. They protect the polymer material from degradation through processing and manufacturing conditions, against sunlight, heat and oxygen exposure which would cause changes of the properties like color, barrier function and physical state. There are several classes of additives which can also be polymeric or oligomeric. Examples are hindered-amine light stabilizers (HALS) which protect the polymer from UV radiation through radical scavenger ability like Tinuvin 622, Chimassorb 944 and Chimassorb 2020 or plasticizers for PVC for example polyadipates (Biedermann & Grob, 2006; Coulier, Kaal, Tienstra, & Hankemeier, 2005).

Analysis of polymeric additives has the same requirements and characteristics as the analysis of oligomers derived from the packaging with the major advantage that the structure of the oligomers is largely, if not completely known. In most cases oligomeric mixed standards are available which facilitates identification and quantification. A further in-depth treatment of polymeric additives is not provided here.

6. Conclusion

Identification and quantification of oligomers is an increasingly food safety relevant and analytically challenging task due to (i) existing knowledge gaps of the toxicological properties of oligomers and (ii) the rising number of different (co)monomers used in the polymer production. To evaluate a polymer regarding its oligomer content and migration potential several factors like isolation of the oligomers from the material, appropriate identification of the oligomer, choice of separation and detection method for quantification, availability of a pure standard or standard analog and possible interferences with other substances present in the sample have to be considered. In general, modern coupled LC-MS techniques have been shown to represent the analytical approach of choice. Indeed, identification of oligomers is mostly accomplished by mass spectrometry since the masses of possible oligomeric compounds are theoretically known from the knowledge of the monomer units. Consequently oligomer libraries could be built up by laboratories to simplify identification.

It may occur that oligomers of different structures possess the same molecular mass. This makes an unambiguous structure assignment of the individual oligomer species very difficult. Ion Mobility as a new separation technique where molecules are differentiated according their drift time depending on their molecular cross-section size could help to assign different oligomeric isomers from the same polymer. The potential selectivity provided by the additional separation dimension of this method might be able to separate isomeric oligomers prior to mass spectrometric analysis.

From a food legislation point of view, oligomers are not treated separately as an own class of chemical substances in the current EU regulations relevant for food contact plastics. However, according to article 3 of the EU Framework Regulation no. 1935/2004 their occurrence in plastics has to be risk assessed. For proper risk assessment, however, sufficiently substantiated toxicological profiles of the oligomeric species would be needed. Safety assessment of oligomers, as far as they can be physiologically degraded back into their monomers, was and is in most cases based on the toxicity data of the respective monomeric components or the monomers'
The most eminent analytical approach or even method can be used for oligomers supported also from an analytical point of view, since the same oligomers as a polymer specie. Due to similar properties of a homologue series of quanti-chromophoric group, a more simple and convenient total oligomer to the substance. In many cases, where a monomeric unit contains a degradation through hydrolysis or thermal and thermo-oxidative processes still might form oligomers as potential migrants from food contact material.

Table 2

<table>
<thead>
<tr>
<th>Polymer sample</th>
<th>Oligomer</th>
<th>Food simulant/ Conditions</th>
<th>Quantification method</th>
<th>Migration value</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tinplate coated with polyester-urethane type I</td>
<td>Cyclic oligoesters below 1000 Da</td>
<td>95% Ethanol</td>
<td>ELSD</td>
<td>0.81 mg/dm²</td>
<td>(Schaef, Ohm et al., 2004)</td>
</tr>
<tr>
<td>Tinplate coated with polyester-phenolic type II</td>
<td>Cyclic oligoesters below 1000 Da</td>
<td>95% Ethanol</td>
<td>UVD</td>
<td>0.47 mg/dm²</td>
<td>(Schaef, Ohm et al., 2004)</td>
</tr>
<tr>
<td>Tinplate coated with polyester-phenolic type III</td>
<td>Cyclic oligoesters below 1000 Da</td>
<td>95% Ethanol</td>
<td>UVD/MSD</td>
<td>0.55 mg/dm²</td>
<td>(Schaef, Ohm et al., 2004)</td>
</tr>
<tr>
<td>Nylon 6 film 15 μm</td>
<td>Cyclic Nylon 6 oligomers n = 1–8</td>
<td>Water</td>
<td>1 h/100 °C</td>
<td>UV</td>
<td>0.46 mg/dm²</td>
</tr>
<tr>
<td>Nylon 6 film 80 μm</td>
<td>Cyclic Nylon 6 oligomers n = 1–8</td>
<td>Water</td>
<td>1 h/100 °C</td>
<td>UV</td>
<td>0.10 mg/dm²</td>
</tr>
<tr>
<td>Nylon 6/66 oven roasting Bag</td>
<td>Nylon 6 oligomers n = 1–4; Nylon 6,6 oligomers n = 1–2</td>
<td>Oil</td>
<td>30 min/176 °C</td>
<td>UV</td>
<td>2.4 mg/dm²</td>
</tr>
<tr>
<td>Nylon 6/66 microwave and roasting bag</td>
<td>Nylon 6 oligomers n = 1–7; Nylon 6,6 oligomers n = 1–3</td>
<td>Oil</td>
<td>1 h/175 °C</td>
<td>UV</td>
<td>0.12 mg/dm²</td>
</tr>
<tr>
<td>Nylon 6/66 microwave and roasting bag</td>
<td>Nylon 6,6 monomer + nylon 6 dimer bag</td>
<td>Chicken</td>
<td>2 h/200 °C</td>
<td>UV</td>
<td>0.9 mg/dm²</td>
</tr>
<tr>
<td>Nylon 6/66 microwave and roasting bag</td>
<td>Nylon 6,6 dimer bag</td>
<td>Chicken</td>
<td>2 h/200 °C</td>
<td>UV</td>
<td>1.86 mg/g</td>
</tr>
<tr>
<td>PET susceptor tray PET cyclic oligomers n = 3–8</td>
<td>Corn oil</td>
<td>3 min/577 W</td>
<td>UV</td>
<td>0.011 mg/dm²</td>
<td>(Begley &amp; Holfild, 1990)</td>
</tr>
<tr>
<td>PET roasting bag</td>
<td>PET cyclic oligomers n = 1–5</td>
<td>Olive oil</td>
<td>7 min/850 W</td>
<td>UV</td>
<td>2.7 mg/dm²</td>
</tr>
</tbody>
</table>

References


Bjarnason, L., Macpherson, A., & Hollander, D. (1995). Intestinal permeability – an structural class. On the other hand, cyclic polycondensate type oligomers can be produced during the manufacture which might require a similarity of homologous chains with a coinciding oxant profile. For groups of migrating oligomers toxicological evaluation has implicitly an additional challenge. The difficulty lies in the huge number of oligomers and the impossibility to obtain a necessary pure amount of each oligomer for toxicological testing. Several approaches for the risk assessment of oligomers have been proposed and applied: evaluation according to the concept of Threshold of Toxicological Concern (TTC) (Cramer, Ford, & Hall, 1976), toxicological testing of the oligomers (Nelson et al., 2011) or subjection of oligomers to physiological digestive solutions simulating (Hamdani, Thil, Gans, & Feigenbaum, 2002) and toxicological evaluation of the reaction products.
Kim, D.-J., & Lee, K.-T. (2012a). Analysis of specific migration of monomers and oligomers from polyethylene terephthalate bottles and trays according to the testing methods as prescribed in the legislation of the EU and Asian countries.


