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Environmental exposure assessment of polymers

TOWARDS A FRAMEWORK FOR ENVIRONMENTAL FATE AND EXPOSURE

ASSESSMENT OF POLYMERS

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Abstract: Development of risk assessment methodologies for polymers is an emerging regulatory priority in order to prevent negative environmental impacts; however, the diversity and complexity of polymers requires adaptation of existing environmental risk assessment approaches. The present review discusses the challenges and opportunities for the fate and exposure assessment of polymers in the context of regulatory environmental risk assessment of chemicals. The review discusses the applicability and adequacy for polymers of existing fate parameters used for non-polymeric compounds, and proposes additional parameters that could inform the fate of polymers. The significance of these parameters in various stages of an exposure assessment framework is highlighted, with classification of polymers as solid or dissolved being key for identification of those

parameters most relevant to environmental fate. Considerations to address the key
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limitations and knowledge gaps are then identified and discussed, specifically: the complexity of polymer identification, with the need for characterisation of the most significant parameters for polymer grouping and prioritisation; the complexity of polymer degradation in the environment, with the need to incorporate the fate and hazards of degradation products into risk assessment; the requirement for development and standardisation of analytical methods for characterisation of polymer fate properties and degradation products; and the need to develop exposure modelling approaches for polymers.

KEYWORDS

ecological risk assessment, environmental fate, microplastics, contaminants of emerging concern, environmental exposure assessment, nanoplastics

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INTRODUCTION

The prevalence and persistence of polymers in the environment has resulted in heightened concern in public, scientific and regulatory communities. Polymers have previously been subject to reduced regulatory requirements compared to low molecular weight (LMW) chemicals, for example under REACH (European Parliament and Council (EP&C) 2006), and there have increasingly been calls for regulation and efforts to develop risk assessment approaches for polymers (European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC) 2019). In particular, the potential risks of plastics and microplastics have been the focus of a vast amount of research due to their widespread release into, and persistence in, the environment (Derraik 2002; Thompson et al. 2009; Ivleva et al. 2017; Koelmans et al. 2017; Burns and Boxall 2018), with a

number of risk assessment strategies being suggested for microplastics (Syberg et al. 2015; Hüffer et al. 2017; Gouin et al. 2019). However, microplastics represent a single group of polymeric material, and in contrast, the environmental impacts of other groups including water-soluble polymers have been given considerably less attention (e.g. Xiong et al. 2018a; Arp and Knutsen 2020). Water-soluble materials were excluded from the definition of microplastics in the recent European Chemicals Agency (ECHA) report for restriction of intentionally added microplastics (ECHA 2019), which could lead to the potential environmental impacts of water-soluble polymers being overlooked. This is despite the fact that water-soluble polymers have many applications, including in agriculture, wastewater treatment, consumer products, and detergents (Arp and Knutsen 2020), and it is inevitable that they will be released to the environment. Additionally, standard exposure and risk assessment protocols for polymers are only just being developed (ECETOC 2019), and technical limitations exist in the tools and methods necessary to support such assessments (ECETOC 2020).

Typically, environmental exposure to chemical substances is assessed using a combination of data on chemical emissions, physicochemical properties, and fate which are then used to inform computational modelling (Di Guardo et al. 2018). However, some of the physicochemical descriptors used to assess the distribution and mobility of LMW chemical substances are not necessarily appropriate for polymers. Moreover, the analytical methods to determine concentrations and properties of LMW chemicals in fate studies may be insufficient for characterisation of polymers. Polymers may also fall outside the applicability domain of many of the models used to support environmental exposure assessment.

Given the previous lack of regulation of polymers, there is a pressing need to establish robust methodologies and procedures in order to evaluate and mitigate potential environmental impacts of polymers. In the present review, environmental exposure assessment of polymers will be discussed in the context of established chemical risk assessment methodologies, in response to increasing urgency to regulate polymers and develop risk assessment approaches. The objectives are to:

- 1) briefly discuss current approaches to prospective environmental risk assessment of chemicals, which include key fate parameters (describing basic physicochemical properties, partition coefficients, bioconcentration and bioaccumulation, and abiotic and biotic degradation), in the context of their applicability to polymers
- 2) assess the significance of these parameters for development of an environmental exposure assessment framework for polymers
- 3) highlight key challenges and considerations for development and application of such assessments to polymers, including polymer identification, polymer degradation, techniques for analysis, and exposure modelling
- 4) identify priorities and future research needs based on the above considerations.

CURRENT APPROACHES TO ENVIRONMENTAL EXPOSURE ASSESSMENT

Exposure assessment is key in environmental risk assessment (ERA), with exposure predictions being combined with ecotoxicity data to determine risk, often by calculation of a risk quotient (RQ) using predicted environmental concentration (PEC) and predicted no-effect concentration (PNEC) (Amiard and Amiard-Triquet 2015).

Key to exposure assessment is the generation of information on the physicochemical properties and fate of a substance. These fate parameters include basic physicochemical

properties such as water solubility, partition coefficients, bioconcentration and bioaccumulation factors, and biotic and abiotic degradation rates, with standard OECD (Organisation for Economic Co-operation and Development) test methods for their measurement.

As experimental fate and property data are sometimes only available for a small proportion of chemical substances in use, structure-activity relationships (SARs) and quantitative structure-activity relationships (QSARs) are often utilised where the data are insufficient or unavailable. QSAR models such as those in the EPI Suite have been established for prediction of physicochemical properties (e.g. water solubility, vapour pressure, Henry's Law Constant, octanol-water partition coefficient) and environmental fate parameters (e.g. degradation half-lives and sorption coefficients) of chemicals (USEPA 2012).

Both experimental and predicted property and fate parameters can ultimately be used as input parameters in exposure models. A multitude of exposure models exist for chemical compounds including very simple lower tier models through to complex higher tier models. Examples include The OECD Tool, a consensus model for ranking overall persistence and long-range transport potential of organic chemicals (Wegmann et al. 2009), EUSES (Vermeire et al. 1997), which may be used to quantify exposure and risk of chemicals (e.g. under REACH), and the FOCUS (FORum for the Co-ordination of pesticide fate models and their USe) models for estimating concentrations of plant protection products (FOCUS 2001). Lower tier models are often very simplistic and provide 'worst-case' concentrations in the environment, often ignoring dissipation processes. Higher tier exposure models typically may rely on a large number of input

parameters including partition coefficients and degradation half-lives in different media, and aim to characterise transport and transformation of a chemical before its ultimate degradation, uptake, or sequestration (Di Guardo et al. 2018).

These different methods for measuring or estimating the properties and fate of molecules and for modelling exposure concentrations may however not be appropriate for polymeric substances. In the following sections, we therefore discuss why polymers are different and assess the validity of these existing methods for exposure assessment of polymers, before then proposing strategies that could be used for polymer exposure assessment.

WHAT ARE POLYMERS AND WHY DO THEY REQUIRE A DIFFERENT APPROACH?

Polymers are typically high molecular weight (HMW) molecules made up of repeating subunits ('monomers'). Fundamentally, they have been defined by the OECD as having a simple weight majority of molecules comprising at least three monomer units bound to another reactant or monomer unit, and a distribution of molecular weights (MW) with less than a simple weight majority of molecules of the same MW, where differences in MW are primarily due to differences in the number of monomer units (OECD 1991). Polymer MW is therefore typically defined in terms of number and weight average molecular weight (MW_N and MW_W , respectively) and molecular weight distribution (MWD). Polymers have widespread usage and are released to the environment both in solid form (e.g. plastics; Kawecki and Nowack 2019) and dissolved form (e.g. from water treatment and agriculture; Arp and Knutsen 2020).

There are a number of unique characteristics of polymers that require additional consideration in exposure assessment compared to LMW chemicals. Polymers often comprise multiple components (including residual monomer, oligomers, polymer chains of varying MW, and chemical additives) and are poorly defined compared to most simple LMW chemical compounds. For example, for polymers (alcohol ethoxylates, alcohol ethoxysulfates, and polycarboxylates) incorporated in the Human & Environmental Risk Assessment on ingredients of European household cleaning products (HERA), in addition to molecular weight distribution for each MW_N , polymers of a wide range of MW_N were in use, with different fate properties (such as degradation and sorption) requiring separate incorporation or consideration in risk assessment (HERA 2004, 2009, 2014a, 2014b). Identification of polymers is complex; names and CAS numbers (which are based on incorporated monomers) are insufficient to differentiate polymers, since the same name and CAS number may apply to two polymers with vastly different properties. Additionally, compared with LMW chemicals, polymers may form a more complex mixture of products when they transform in the environment, including cross-linked polymer chains, micro- and nano-scale particles, oligomers, and LMW chemical compounds (e.g. Saad et al. 2010; Lambert et al. 2013a, 2013b; Ter Halle et al. 2016; Weinstein et al. 2016). It has been highlighted that there has been inconsistency in the size classes used for plastic debris; for the purposes of the present review, the terms ‘macro-polymer’, ‘meso-polymer’, ‘micro-polymer’, and ‘nano-polymer’ will refer to polymeric substances with size ranges of ≥ 10 mm, 1 to <10 mm, 1 to <1000 μm and 1 to <1000 nm, respectively, according to the recommendations given by Hartmann et al. (2019) for plastic debris.

It is likely that for lower tier, worst-case ERA scenarios, existing exposure assessment methods will be generally sufficient for polymers, with only information on usage/production volumes and emissions estimates being necessary, although the availability of this data for many current-use polymers may limit characterisation of exposure (Duis et al. 2021). However, for more complex, higher tier environmental exposure assessment studies which incorporate data on fate behaviour, additional considerations are likely to be necessary for polymers. Only a limited number of environmental exposure and risk assessments have been performed for polymers to date, including for polyethoxylated surfactants, polycarboxylates, and polyquaterniums (e.g. HERA 2004; Cumming 2008; HERA 2009, 2014a, 2014b; DeLeo et al. 2020), with detailed information on polymer characteristics often being limited (Duis et al. 2021). For example, the assessment of polyquaterniums conducted by Cumming (2008) was limited by insufficient information to estimate the mixture of polyquaterniums present, or their range of charge densities and molecular weight.

A primary concern for higher tier environmental exposure assessment is the establishment of key parameters to measure the behaviour and fate processes of polymers in the environment. In the present review, a detailed analysis of the relevance and applicability of fate parameters to polymers has been performed, exemplifying the need for additional considerations in higher tier exposure assessment of polymers and application of fate parameters in exposure modelling. The applicability of established fate parameters for LMW chemical compounds to polymers is first discussed below, and summarised in Table 1. We suggest that both homo- and co-polymers can be grouped either as solid polymers (including bulk macroscopic solids and particles) or dissolved

polymers (defined in the present review to cover polymers which are dissolved in solution, such as water-soluble polymers in an aqueous environment, and polymers which exist in the liquid state (which may be water-insoluble)), based on applicability of both established fate parameters and suggested polymer-specific parameters. This grouping underpins the following discussion.

Basic physicochemical properties

Boiling points (T_b) are typically not relevant for most polymers, since, by definition, polymers exist as macromolecules with high molecular weights, and typically decompose before boiling (e.g. Schupp et al. 2018). Similarly, vapour pressure (P) will generally remain low for dissolved polymers due to their high molecular weight. Whilst vapour pressure can be measured for some liquid polymers, it is likely that it is LMW and oligomeric components that contribute most to the vapour pressure (Schupp et al. 2018); P may therefore be a relevant parameter for some LMW polymers and substances containing high levels of oligomers or residual monomer (RPA/GnoSys/Milieu 2012).

Conversely, melting points (T_m) are applicable to both LMW and HMW polymers. In the context of polymers, the melting temperature refers to the transition between crystalline and amorphous states, and applies only to semi-crystalline polymers (Alsleben and Schick 1994). The physical properties of the polymer matrix in a solid polymer may play an important role in environmental fate and effects. For example, LMW constituents may leach more readily from a flexible polymer compared to a rigid one (Hoekstra et al. 2015), and amorphous polymers or polymer regions may undergo preferential (bio)degradation before those that are crystalline structured (Khatriwala et al. 2008; Fukushima et al. 2013).

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Reactive functional groups (RFGs) also influence environmental fate, and in contrast to LMW chemical compounds, the functional group equivalent weight (FGEW) is important for polymers, as it describes the relative proportion of RFGs within the polymer (ECETOC 2019). Anionic and cationic polymers are analogous to acidic and basic polymers, respectively (e.g. Guiney et al. 1998; Ostolska and Wiśniewska 2014; Hennecke et al. 2018) and measurement of their $pK_a(s)$ can enable prediction of their charge or charge distribution (q) at environmental pH (e.g. Schupp et al. 2018). Ionic polymers have multiple applications, including in household products (Pecquet et al. 2019) and wastewater treatment (e.g. Shen et al. 2013), and there has been concern over the ecological hazard potential of cationic polymers (e.g. Goodrich et al. 1991; USEPA 1997; Cumming et al. 2008; Costa et al. 2014). Charge also influences environmental fate processes such as sorption (Galvão et al. 2007; Blachier et al. 2009). Surface tension (γ) is relevant for dissolved and colloidal polymers with surfactant properties, with surfactant behaviour being recognised as significant for environmental fate and effects (e.g. Jardak et al. 2016).

Partition coefficients

Parameters such as the soil/water and soil organic carbon/water partition coefficients (K_d and K_{oc} , respectively; Kookana et al. 2014), are used to assess the partitioning of chemicals between soil/sediment/sludge and water (Amiard and Amiard-Triquet 2015), and are useful in predicting the concentrations of a chemical in these environmental compartments. Although terrestrial environments and soils are an important receiving compartment of both solid and dissolved polymers (due to application of, for example, sludge, mulch, agrochemicals, and soil conditioners; Felsot et al. 2011; Horton et al.

2017; Arp and Knutsen 2020), the use of K_d and K_{oc} in the context of bulk solid polymers is not appropriate. As has been highlighted in the literature, colloidal dispersions do not reach thermodynamic equilibrium. Instead, processes such as sorption to soils are kinetically controlled, and are dependent on time, concentration, and system conditions (Kookana et al. 2014; Praetorius et al. 2014). It therefore follows that application of K_{oc} and K_d , as well as other commonly used equilibrium-based partition coefficients such as the octanol-water partition coefficient (K_{ow}) to partitioning of nano-sized polymer particles, as well as micro-scale particles and larger solids which can undergo sedimentation, is not appropriate and may lead to erroneous results (Praetorius et al. 2014). Such equilibrium-based partitioning parameters should only be applied to polymer molecules, not bulk solids (e.g. Min et al. 2020).

These parameters may therefore be applied to dissolved polymers, as these will follow equilibrium partitioning behaviour. Equilibrium partition coefficients have been previously applied to polymer macromolecules (Gorbunov and Skvortsov 1995; Tong and Anderson 1996; White and Deen 2000; Lazzara and Deen 2004), usually in the context of partitioning between a gel and solution, but also in an environmental context, albeit rarely (Cumming et al. 2011a; Cumming et al. 2011b). However, use of K_{ow} to indicate potential for bioaccumulation may be insufficient for HMW polymers due to uptake by non-partitioning processes (see later discussion of bioconcentration and bioaccumulation). Given that polymer molecules in solution can also exist in the nano-size range (Armstrong et al. 2004; Xiong et al. 2018b; Arp and Knutsen 2020), it may also be relevant to test and verify the applicability domain of equilibrium-based parameters to such polymers. Furthermore, as has been discussed by Cumming (2008)

and Duis et al. (2021) in the context of environmental fate of polyquaterniums, polyethylene glycols, and acrylic acid polymers, conformation of polymer chains is likely to play a role in sorption and desorption, which will affect partitioning to soils and sediment in the environment for dissolved polymers.

Bioconcentration and bioaccumulation

Bioconcentration and bioaccumulation factors (BCF and BAF, respectively) are often used in fate and hazard assessment of chemicals (e.g. Berrojalbiz et al. 2009; Wu et al. 2011; Castro et al. 2019) to characterise uptake and accumulation into organisms in the environment. Whilst BCF accounts for uptake of a chemical substance only via dermal and respiratory absorption, BAF accounts for additional uptake via ingestion (Arnot and Gobas 2006; Mackay et al. 2013). Since the concept of BCF assumes passive diffusion, it is known to be inapplicable to nanoparticles (Kookana et al. 2014; Kühnel and Nickel 2014), as equilibrium partitioning does not apply and active processes such as endocytosis play a significant role in nanoparticle uptake due to their size (Fröhlich 2012; Kookana et al. 2014; Utembe et al. 2018). This is also the case for larger solids such as microplastics (von Moos et al. 2012). The role of active processes also means that BCF and BAF may be dependent on exposure concentration and thus differences between substances cannot only be attributed to differences in bioaccumulation (Utembe et al. 2018). It has been highlighted that parameters such as uptake and internalisation rates and attachment efficiencies (α) should be identified and developed for nanoparticle bioaccumulation (Kühnel and Nickel 2014; Praetorius et al. 2014). Test methods based on concentrations and rate constants may need to be modified and should be interpreted such that they reflect uptake/depuration rates rather than BCF (Kookana et al. 2014);

uptake and depuration rate constants (k_u and k_d , respectively), as well as assimilation efficiency (AE), have been applied to nanoparticles previously (Zhao and Wang 2010; Dai et al. 2015).

Knowledge from medicinal chemistry shows that endocytosis also plays a role in cell uptake of polymer molecules (Apostolovic et al. 2011) due to their large size, suggesting that BCF and BAF are also likely to be insufficient to describe uptake of dissolved polymers. Polymer and particle properties that influence cell membrane interactions and uptake have been identified from medicinal applications of polymers and nanoparticles in drug delivery, and include size, shape, composition, hydrophobicity, surface charge, and distribution of functional groups (Liechty et al. 2010; Fröhlich 2012). These properties may therefore be important for characterisation of biological fate processes of both solid and dissolved polymers.

Abiotic and biotic degradation

Degradation rates have been often assessed for polymers (e.g. Gómez and Michel Jr. 2013; Lambert et al. 2013a; Auta et al. 2018; Hennecke et al. 2018), and the degradation parameters half-life and degradation rate constant ($t_{1/2}$ and k_{deg} , respectively) remain applicable; however, the increased complexity of polymer degradation mechanisms and products should also be considered. Whilst degradation products of LMW chemicals are routinely incorporated into environmental risk assessments, the number and variety of products formed from polymer degradation may be far greater, potentially including HMW molecules, micro- and nano-scale particles, and oligomers and LMW chemical compounds (e.g. Saad et al. 2010; Lambert et al. 2013a, 2013b; Ter Halle et al. 2016; Weinstein et al. 2016). The complexity of the product mixture from degradation of a solid

polymer along with implications for polymer properties and key fate parameters is illustrated in Figure 1.

Degradation mechanisms and $t_{1/2}$ and k_{deg} values depend on both polymer properties (including the presence of certain RFGs, hydrophobicity, molecular weight, glass transition temperature (T_g), and fragment size, among others; Ter Halle et al. 2017; Min et al. 2020), and environmental factors (including light and oxygen availability, temperature, pH, salinity, and biofilm formation; Lambert et al. 2013a; Da Costa et al. 2018; Morohoshi et al. 2018). Polymer transformation products are likely to have different fate and degradation characteristics compared to one another and to the parent material, which will itself be altered, presenting challenges for characterising potential risk. Standard test methods will require modification and additional analytical techniques to characterise these products and corresponding degradation pathways.

Polymer particles may be formed from breakdown of a solid polymer; in addition, whilst water-soluble polymers are most likely to degrade into oligomers and chemical compounds rather than particles, there has been speculation over the potential for soluble polymers to form insoluble material in the environment (Arp and Knutsen 2020), and it should be noted that polymer solubility does not preclude non-biodegradability and environmental persistence (Swift 1998; Hennecke et al. 2018; Arp and Knutsen 2020). Particles formed from polymer degradation can further fragment or aggregate (Liu et al. 2019); importantly, these secondary particles formed by polymer fragmentation are likely to differ from primary emitted particles such as primary microplastics. They will be more irregular in shape (e.g. Frydkjær et al. 2017), and both primary and secondary particles which have been exposed to the environment may have altered density (Morét-Ferguson

et al. 2010; Chubarenko et al. 2016) and surface properties (Waldman and Rillig 2020), with different RFGs, charge (S_q), and topography (Fotopoulou and Karapanagioti 2012). These changes will influence fate; for example, the surfaces of UV-degraded polystyrene nanoparticles have been shown to be more oxygen-rich, potentially influencing aggregation behaviour compared to non-degraded particles (Liu et al. 2019).

Ultimately, chemical products will form from polymer degradation; several LMW chemical products have been identified from plastic degradation (reviewed by Bond et al. (2018)), and other solid polymers such as latex (Lambert et al. 2013b). Most prioritisation methodologies classify polymers of high average molecular weight ($\geq 1,000$ Da) as low concern (PLC) due to the expectation that they may be less able to cross organism membranes (OECD 2009). However, all polymers have the potential to degrade into LMW species following emission to the environment, with many PLC exclusion criteria acknowledging ‘substantial’ (bio)degradation as indicating potential concern (ECETOC 2019).

Additional parameters for polymer exposure assessment

In addition to the established parameters for LMW chemicals discussed above and summarised in Table 1, it is clear that there are a number of properties of polymers that are not applicable to LMW chemicals, but which may be instrumental in polymer exposure assessment. Suitable parameters and descriptors for such properties are suggested in the present review. A combination of established and novel parameters to describe polymer environmental fate is likely to be necessary, and will again be facilitated by classification of polymers as solid or dissolved. The overall picture is complex, with different sets of parameters likely being key for LMW chemical

compounds, solid polymers, and dissolved polymers. This has been summarised and illustrated in Figure 2.

An obvious distinction of polymers is their distributed MW (OECD 1991), which can be measured in terms of MW_N , MW_W , and MWD. The presence of leachable LMW compounds or oligomers in a polymer is also important, as these may be more bioavailable (e.g. Bejgarn et al. 2015). MW_N , MW_W , MWD, and LMW content of polymers can be characterised using size exclusion chromatography (OECD 1996a, 1996b).

An important property determining fate is solubility. Hildebrand and Hansen solubility parameters (δ) (Miller-Chou and Koenig 2003) have been used to predict polymer solubility in various solvents (Venkatram et al. 2019); however, there are a number of limitations of such methods, and they should be considered only predictive (Venkatram et al. 2019). Experimental determination of a polymer's concentration in solution is critical (OECD 2000; Hartmann et al. 2019). Polymer solubility is also key for their classification within the framework of the present review, along with polymer solidity or hardness; solidity is also significant for the ECHA definition of microplastics as solid (ECHA 2019) and may influence environmental fate (for example by influencing biofilm formation; Muthukumar et al. 2011). Solid polymers also have several properties which are not shared with dissolved polymers but which are likely to be key for environmental fate, including particle size distribution (PSD), shape, surface properties, and aggregation characteristics.

Particle size, for example, will influence environmental fate and may dominate over other parameters such as density. Density (ρ) can be assessed via a number of methods

(OECD 2012a) and can influence position in the water column and settling into sediment in an aqueous environment (Chubarenko et al. 2016). However, in a modelling study, Besseling et al. (2017) found that whilst retention of 1 – 200 μm plastic particles in a river stretch increased with polymer density, retention of 0.1 – 1 μm particles was almost density-independent, instead being driven by particle size. Similarly, some plastic types that are denser than seawater have been found in the form of micro- and nano-particles on the sea surface, suggesting that smaller debris may have different floatation behaviour despite density considerations (Ter Halle et al. 2017). This phenomenon highlights the complexity that can arise through the overlapping influence of multiple fate parameters.

Standard methods for measurement of PSD are based on sedimentation, centrifugation or Coulter Counter, or microscopic techniques for fibres (OECD 1981). Whilst size is most commonly used to refer to solid particles, dissolved polymer molecules may exist in the nano-size range, and thus measurement of hydrodynamic radius (R_h) may be important in characterising their fate. As well as influencing transport and vertical distribution as discussed above, particle size may also influence polymer degradation rate, along with particle shape (Ter Halle et al. 2016). Particle shape may also influence residence time in organisms (Frydkjær et al. 2017), as well as surface area (S_A) and therefore degree of biofouling, which can in turn influence settling time, heteroaggregation, and degradation (Chubarenko et al. 2016; Michels et al. 2018; Morohoshi et al. 2018). Shape and S_A are thus potentially important fate parameters for particles.

Other surface characteristics of particles such as surface charge (S_q) may be important (e.g. Fotopoulou and Karapanagioti 2012). Surface charge of nano-scale polymer

particles in colloidal suspensions can be assessed by measurement of the zeta potential (ζ), which influences stability and therefore aggregation behaviour (Cai et al. 2018; Oriekhova and Stoll 2018; Liu et al. 2019; Saavedra et al. 2019; Wu et al. 2019). Aggregate formation is also key, and may influence vertical transport of polymer particles in the environment (Michels et al. 2018). As described previously, the use of partition coefficients is not relevant to describe partitioning of solid particles via aggregation and deposition. Instead, kinetic parameters such as attachment efficiency (α) can be used (Praetorius et al. 2014). Attachment efficiency has been determined experimentally for analysis of heteroaggregation between microplastics, nanoplastics, and clays (Besseling et al. 2017).

The deposition rate constant (k_{dep}) may also be relevant (along with α) to assess settling times in an aquatic environment when equilibrium partitioning to sediment does not apply. Deposition of airborne polymeric particles in the micro- and nano-range (Bergmann et al. 2019; Kawecki and Nowack 2019; Wright et al. 2020), and dissolved polymers present in aerosols, for example in agricultural sprays (e.g. Felsot et al. 2011; Lewis et al. 2016), may also be significant. The deposition rate constant has been used to describe deposition of engineered nanoparticles both to soil and water from the atmosphere, and to sediment from an aqueous environment (Meesters et al. 2014).

There are other fate properties that may be key to polymer exposure assessment. For example, viscosity (η) (OECD 2012b), also used in environmental fate analyses of oil spills (Sebastião and Soares 1995), may be important for liquid polymers. In addition to T_m , T_g is useful in polymer matrix characterisation as it describes the transition from rigid

and glassy to rubbery, and has been found to influence sorption and desorption of organic contaminants (Teuten et al. 2009) as well as polymer degradation rate (Min et al. 2020).

In addition, metrics for quantifying exposure are key; whilst mass concentration remains sufficient for dissolved polymers, for solid polymers and particles, number concentration and particle size distribution (PSD) are likely to also be significant (Kookana et al. 2014). This is illustrated by the fact that larger particles may dominate in terms of mass, but smaller particles may dominate in terms of number (Ter Halle et al. 2016; Schwaferts et al. 2019), meaning the metric measured may influence conclusions drawn about relative environmental impacts.

Analytical techniques for polymer characterisation

It has been recognised that standard test methods may need to be adapted for application to polymers (ECETOC 2020). Whilst some methods do exist that are specifically tailored to polymers or solids, such as for assessment of solubility, MWD, and PSD (OECD 1981, 1996a, 2000), an array of additional techniques may be required for full characterisation of a polymer. The traditional methodologies used for chemical analysis, including chromatography and mass spectrometry, may need to be adapted or replaced to characterise parameters such as shape, aggregation behaviour, and topography. Additionally, the existence of a ‘methodological gap’ in the nano-size range has been highlighted (Schwaferts et al. 2019), and it has been recognised multiple times in the literature that there is a lack of both standardisation and adequate validation of some techniques for plastic particle analysis (Hidalgo-Ruz et al. 2012; Ivleva et al. 2017; Burns and Boxall 2018; Pico et al. 2019). Knowledge from nanoparticle and microplastic analysis will be invaluable in further developing techniques for polymer analysis in

exposure and risk assessment. Importantly, given the potentially massive range of products that may be formed from polymer degradation, use of a wide array of techniques will most likely be necessary for a single environmental degradation study if all products are to be characterised. Fully characterising the rate, route and products of polymer degradation may therefore be difficult to achieve in a time and cost-effective manner, despite the importance of such studies for environmental risk assessment.

Structure-activity relationships and exposure models for polymers

Given that most QSAR models have been developed specifically for LMW organic compounds, many will be insufficient for application to polymers (ECHA 2016), and prediction of polymer environmental fate should also address additional influences as a result of polymer size, molecular weight, and macromolecular properties. A lack of data on polymer environmental fate will also limit development of polymer QSARs. Although models such as ECOSAR include recommendations for assessing the aquatic hazard of polymers (Mayo-Bean et al. 2017), they are limited by availability of data and have been developed only for specific polymer classes, meaning they are often not applicable to new polymers (Nolte et al. 2017b).

Given the added complexity of polymers compared to LMW compounds and the additional parameters influencing polymer fate, complex exposure models for polymer ERA may also require additional considerations. Whilst many simple, lower tier models are likely to be appropriate for polymers, higher tier models which require fate parameters as inputs may need to be adapted to account for the polymer-specific processes described above. For example, models such as the FOCUS models for pesticides (FOCUS 2001), and the ePiE model developed for pharmaceuticals,

incorporate partition coefficients and loss processes such as degradation (Oldenkamp et al. 2018). However, for a solid polymer particle, partition coefficients are not applicable and degradation processes may not indicate a decrease in exposure, since initial degradation may simply form a larger number of smaller particles. Parameters such as size, shape, density, and attachment efficiencies, among others, will dictate transport and fate of particles (Kooi et al. 2018) in place of partition coefficients. Similarly, given the general lack of fate analyses of dissolved polymers, assessment of the applicability of fate models for LMW chemicals may be necessary, given that parameters such as size, molecular weight, and macromolecular properties such as chain conformation are likely to influence dissolved polymer fate.

TOWARDS A FRAMEWORK FOR POLYMER EXPOSURE ASSESSMENT

To move towards a framework for polymer environmental exposure assessment, we have identified key fate parameters and descriptors that are likely to be most significant (Figure 3). These include key physicochemical properties required for identification and characterisation of polymers, which can also facilitate polymer grouping and prioritisation. Approaches to polymer grouping have been discussed in detail by ECETOC (2019); in the present review we highlight key parameters for polymer characterisation for exposure assessment based on the discussion of fate parameters above, including properties such as molecular weight parameters, solubility, presence of functional groups, and transition temperatures.

We have also identified the most relevant parameters for higher tier exposure modelling (Figure 3), and recommend that classification of polymers in terms of whether they will be in dissolved or solid form is likely to be useful in environmental risk

assessment, since this will define the relevance of all other fate parameters to the polymer in question. This is particularly relevant for in-depth exposure assessment, to focus assessment efforts and avoid incorrect application of parameters. Whilst parameters such as k_{deg} , $t_{1/2}$, and many of the key physicochemical properties identified previously will be relevant to both groups, properties such as PSD, attachment efficiencies, and surface properties are unique to solid materials, and equilibrium partition coefficients are only applicable to dissolved polymers. It is important to note that development of analytical techniques is key moving forward, both for monitoring studies and in characterisation of key parameters for polymers.

From this framework (Figure 3), key considerations to address the knowledge gaps discussed previously can be identified, including: the most important parameters for polymer identification, grouping, prioritisation, and fate analysis; complex degradation processes and byproducts of polymers; available analytical techniques for polymer analysis; and fate and exposure modelling of polymers. These considerations are addressed in the context of the exposure assessment framework (Figure 3) below.

CONSIDERATIONS AND KEY RESEARCH NEEDS FOR POLYMER EXPOSURE AND RISK ASSESSMENT

Key parameters for polymer identification, grouping, and environmental fate

There is a clear need to develop standard identifiers for polymers to avoid ambiguity in risk assessment; identifiers based on the key physicochemical properties summarised in Figure 2 may be useful in differentiating polymers formed from the same monomer units, which would otherwise not be distinguishable from just, for example, name and CAS number. A number of these descriptors have also been highlighted by ECETOC

(2019), including molecular weight (MW_N , MW_W , MWD), T_m , T_g , and solubility, among others.

However, it is still unclear which parameters may be most important for polymer grouping and exposure assessment, given the complexity and potential overlap of factors in influencing environmental behaviour. Development of grouping approaches based on correlation between key parameters and environmental behaviour is necessary, which will likely require data from experimental fate and ecotoxicology studies for a wide range of polymers. Assessing the ability of key parameters to predict environmental behaviour of polymers is likely to be achieved through a combination of experimental fate studies and modelling; for example, Min et al. (2020) established key predictors for surface erosion and degradation of marine plastic debris based on physical properties and molecular structure. Similar analyses for other polymers and endpoints, based on use of experimental data, intrinsic properties, and key parameters to inform predictive modelling, are likely to be extremely useful in environmental exposure assessment and grouping. Further research into the relative extent that certain properties may influence hazard and fate, with establishment of a hierarchy of features to predict environmental behaviour (Min et al. 2020), as well as how these properties may interact to mitigate or exacerbate hazard, is warranted. Filling this research gap would also supplement development of QSARs and read-across approaches, as well as prioritisation efforts for polymers and identification of data needs for risk assessment. Development of QSARs for polymers will also further consolidate grouping approaches and establishment of key parameters for environmental exposure assessment of polymers.

Research into cut-off points for solidity and solubility is also warranted given the potential ambiguity that may arise for polymers which are not clearly either solid or dissolved (e.g. waxes). For polymers of sufficiently low molecular weight, parameters that would normally only be relevant for LMW chemical substances and oligomers (such as P and BCF) may become relevant, and so it may be important to define molecular weight cut-off points for such parameters. Additionally, as knowledge develops of which properties of particles may confer hazard, such as shape and surface properties (e.g. Della Torre et al. 2014; Frydkjær et al. 2017), the relative importance of these parameters for grouping of micro- and nano-polymers may become apparent.

Polymer degradation and implications for fate

Many of the current standard test methods for degradation study different transformation pathways in isolation or under specific sets of conditions (e.g. OECD 2004a, 2008); however, it is likely that in the environment these processes will occur in tandem and may interact. Therefore, use of simulation tests which closely mimic environmental conditions (e.g. OECD 2004b), in order to study net degradation processes and products, are likely to be more useful in characterising complex polymer degradation. Such tests are frequently employed in environmental exposure assessment, and have been applied to a number of polymer classes. In particular, environmental exposure and risk assessments have been conducted for alcohol ethoxylates, alcohol ethoxysulfates, and polycarboxylate homo- and co-polymers as part of the HERA project (HERA 2004, 2009, 2014a, 2014b), with degradation data for these classes of polymers being summarised as part of these risk assessments. In addition, Duis et al. (2021) gathered available data for several polycarboxylate polymers, polyethylene glycols, and polyquaterniums.

In the present review, we have further summarised the aforementioned collated degradation data for these polymer types, in order to provide a comprehensive overview of the available degradation data and test results for these polymers, presented in Table 2. Full details are presented in the Supporting Information. We have here focussed on available data relevant to environmental exposure assessment for water-soluble polymers, given the vast pool of studies available on degradation of marine plastic debris which frequently employ varied and non-standard methods.

Whilst there are degradation data in a range of media available for many of these polymer groups (Table 2), it should be noted that these groups cover only a small fraction of the polymer types in current use, and degradation data for environmental matrices (surface waters, soils, and sediments) are limited. There are also little data available for polyquaterniums as a class (Duis et al. 2021), despite potential concerns relating to environmental hazard of cationic polymers (e.g. USEPA 1997). In addition, a lack of availability of information on experimental methods limits assessment of the quality of some results (Duis et al. 2021) as well as comparison and verification between studies, highlighting the need for transparency and standardisation of methods for adequate risk assessment.

In general, it can be observed that alcohol ethoxylates, alcohol ethoxysulfates, and polyethylene glycols often exhibit higher rates or levels of degradation than polycarboxylates and polyquaterniums, although there are high levels of variation due to the wide ranges of polymers summarised together in the present review. Importantly, many studies focus on extent of degradation and associated biodegradability endpoints (Table 2), whereas full environmental exposure assessment will in many cases require

treatment of degradation products formed. In addition, tests focussed on measures such as CO₂ evolution may underestimate degradation for some HMW polymers which may undergo extensive fragmentation into lower MW polymer chains before complete mineralisation; similarly, measurement of loss of a parent material may overlook the presence of persistent polymer chains of lower MW. Analysis of degradation products will likely require additional parameters and a wide array of analytical techniques to describe their fate. However, it may not always be feasible to characterise the full range of polymer degradation products, particularly given the constraints of current analytical methodologies for analysis of nano-scale polymer particles; therefore, further research into optimum methods by which polymer degradation can be characterised, which product types are most significant in terms of environmental risk, and how polymer properties can be predictive of degradation products (e.g. Min et al. 2020), is warranted.

Characterisation of polymers and degradation products

A further key consideration for polymer exposure assessment is the analytical tools available to characterise polymer fate and degradation processes. The applicability of existing standard test methods to analysis of polymer properties and fate parameters has been evaluated (ECETOC 2020), and thus in the present review we present a holistic overview of how analytical tools could be deployed and further developed to better characterise polymer specific fate properties and degradation products.

Fate and degradation studies may involve use of complex environmental matrices, which will often require extraction or separation prior to analysis. A number of methods exist for extraction of micro- and nano-plastics from soils, sediments, and biota, including density separation and chemical or enzymatic digestion (e.g. Karlsson et al.

2017; Hurley et al. 2018). However, these treatments may alter the particle analytes (Enders et al. 2017; Rist et al. 2017; Hurley et al. 2018), and thus methods should be tested and validated for the polymers in question. For analysis of LMW chemical compounds in complex environmental matrices, various solvent extraction techniques are typically used (e.g. Basheer et al. 2005; Martínez-Parreño et al. 2008; Berlioz-Barbier et al. 2014), which may be developed and optimised for dissolved polymers (e.g. Antić et al. 2011).

A number of reviews of available techniques for analysis of micro- and nano-plastics in the environment are available (Li et al. 2018; Silva et al. 2018; Nguyen et al. 2019; Schwaferts et al. 2019; Fu et al. 2020). The advantages and limitations of some key analytical methods for solid polymers and their degradation products are summarised in Table 3 and further discussed below.

Microscopy, particularly light microscopy and scanning electron microscopy (SEM), is commonly used in visualisation of plastics, allowing characterisation of size and shape of particles (e.g. Ter Halle et al. 2016; Hernandez et al. 2017; Oriekhova and Stoll 2018) and surface degradation of macro-polymers (Gómez and Michel Jr. 2013; Musioł et al. 2017). However, unequivocal chemical identification of the analyte is essential, and relies on combination with spectroscopic methods such as Fourier-transform infra-red (FTIR) and Raman spectroscopy (Burns and Boxall 2018; Cabernard et al. 2018), which may also provide information on chemical changes with degradation (Da Costa et al. 2018). Automation can provide faster and more reliable results, and reduce issues with bias and sample representativeness, for example in focal plane array (FPA)-based micro-FTIR

(Löder et al. 2015; Primpke et al. 2017). However, spectroscopic techniques are unable to give chemical information on particles below the micro-scale.

Information on PSD can also be obtained from scattering or diffraction-based techniques, which can be applied to nano-scale particles (e.g. Gigault et al. 2016; Lambert and Wagner 2016a; Mintenig et al. 2018). Laser diffraction (LD) instruments in particular have the potential to cover a wide particle size range (Witt and Röthele 1996; Keck and Müller 2008), and dynamic light scattering (DLS) and nanoparticle tracking analysis (NTA) are useful for characterising particle aggregation (e.g. Filipe et al. 2010; Besseling et al. 2017; Gigault et al. 2017). However, such techniques typically utilise spherical models to describe particles (e.g. Eshel et al. 2004; Lambert and Wagner 2016b; Frydkjær et al. 2017) which may influence analysis of irregularly-shaped secondary particles. Techniques such as DLS and multi-angle light scattering (MALS) may also require pre-separation of particles into specific size fractions, which can be achieved using asymmetric flow field-flow fractionation (AF4) (e.g. Filipe et al. 2010; Gigault et al. 2017; Mintenig et al. 2018); however, it has been highlighted that many AF4 techniques have been optimised using primary particles, and secondary particles may behave differently (Schwaferts et al. 2019). Chromatographic techniques utilised in nanoparticle separation and analysis that have the potential to be adapted for plastic particle analysis have also been highlighted by Schwaferts et al. (2019), including hydrodynamic chromatography (HDC) and high-performance liquid chromatography (HPLC).

For chemical analysis of nano-sized particles, mass spectrometry techniques are crucial. Pyrolysis gas-chromatography mass-spectrometry (py-GCMS) has been used to

identify polymer types of plastic particles (Fries et al. 2013; Ter Halle et al. 2017; Hermabessiere et al. 2018), and may reveal changes resulting from degradation (Ter Halle et al. 2017). Thermal extraction desorption gas-chromatography mass-spectrometry (TED-GCMS) can be used to directly analyse and potentially quantify plastic particles in an environmental sample (Dümichen et al. 2014; Dümichen et al. 2015; Dümichen et al. 2017; Dümichen et al. 2019), making it a potentially powerful technique for analysis of polymers in environmental matrices in fate and degradation studies.

Other techniques are available to determine additional key properties for polymer fate analysis. For example, molecular weight information can be obtained using gel-permeation chromatography (GPC), which has been used in analysis of microplastics down to 10 μm (Hintersteiner et al. 2015). Differential scanning calorimetry (DSC) can give information on thermal properties including T_m and T_g (Deroiné et al. 2014; Musioł et al. 2017).

Whilst most studies have focussed on analysis of solid plastic polymers, particularly microplastics, most chemical identification techniques will also be suitable for dissolved polymers, as highlighted by Arp and Knutsen (2020). Additionally, scattering methods have been used to characterise the hydrodynamic radius of polymers in solution (Armstrong et al. 2004). However, whilst some analyses of water-soluble polymers in environmental matrices have been carried out (e.g. Antić et al. 2011), overall few techniques have been developed for environmental analysis of dissolved and water-soluble polymers (Huppertsberg et al. 2020), presenting a key research need for environmental exposure assessment.

Each technique has a workable size range (Figure 4) and provides different levels of information, emphasising the importance of addressing the research need in question (Elert et al. 2017). It is likely that full characterisation of a polymer and its degradation products for fate and exposure assessment will require a combination of techniques which should be tailored to the nature of the polymer in question. For a solid polymer, this may include all or a combination of chromatographic, spectroscopic, scattering, and spectrometric techniques. For example, Mintenig et al. (2018) recently combined AF4-MALS with py-GCMS to characterise both particle size and polymer type of nanoplastics in environmental samples within a suggested framework for micro- and nano-plastic analysis. Use of multiple techniques may aid in analysis of diverse polymer degradation products in standard degradation tests when characterising full rate and route (e.g. OECD 2002, 2008) as well as facilitating development of new standard test methods for polymer-specific properties and fate parameters. For example, DLS and spectrophotometry may be useful in establishing standardised methods for determining α of polymer particles to describe aggregation with suspended particles (Besseling et al. 2017) as an alternative to partition coefficients. However, the need for full sample characterisation should be balanced with time and cost-effectiveness, and the level of information needed for adequate risk assessment. As methods and data relating to polymer risk assessment continue to develop, the key properties, polymer types, and degradation products dictating fate and hazard may be elucidated and used to refine and focus risk assessment methodologies and analytical technique development. Analytical techniques developed for nanoparticles and microplastics will be useful in solid polymer risk assessment; however, it has been recognised that a previous lack of standardisation

and adequate quality control of techniques for microplastic analysis has hindered progress in assessing their environmental risk (Burns and Boxall 2018). Moving forward in polymer analysis, further development and standardisation of techniques is required for robust risk assessment methodologies, with improvement and adaptation of the techniques discussed in the present review as well as development of novel methods likely being necessary.

Fate and exposure models for polymers

Given the differences in applicability and importance of fate parameters to polymers compared with LMW compounds, development of methods for prediction of fate properties as well as higher tier exposure models for polymers which incorporate both measured and predicted fate parameters is warranted. Whilst some efforts have been made to predict environmental fate of polymers based on their intrinsic properties (Min et al. 2020) and QSARs have been developed for algal toxicity of polymer particles (Nolte et al. 2017b), further development of robust datasets for model development to establish an array of QSARs for polymer environmental fate is warranted. Adaptation of QSARs for engineered nanoparticles may also be useful for application to polymer particles.

Exposure models for engineered nanoparticles have now been developed, and range in complexity from emission-based mass-balance models (e.g. Gottschalk et al. 2009) to multimedia (e.g. Meesters et al. 2014) and spatiotemporally resolved (e.g. Quik et al. 2015; Domercq et al. 2018). Recently, fate models have also been applied to micro- and nano-plastics (e.g. Nizzetto et al. 2016; Besseling et al. 2017), with the unique combination of low density, wide size range, persistence, and variable shape of plastic particles distinguishing them from other particle types in fate and exposure modelling

(Kooi et al. 2018). Research on environmental exposure to dissolved polymers remains scarce, and exposure models may again require development of additional input parameters, given the additional properties of polymers which are not applicable to LMW chemical compounds.

CONCLUSIONS AND RECOMMENDATIONS

Given the widespread and increasing use of both solid and liquid or water-soluble polymers, and their subsequent release into the environment, development of environmental risk assessment approaches is essential. The unique and complex nature of polymers, including their high and distributed molecular weights, potentially complex matrix properties, and the presence of various additives, means that adaptation of current risk assessment approaches is warranted.

In environmental exposure assessment, use of key fate parameters is essential for fate characterisation and modelling; however, some parameters established for LMW chemical compounds are unlikely to be relevant to polymers. In the present review, an assessment of the relevance of typically used fate parameters to polymers has been performed, revealing that solidity and solubility of polymers are key to the applicability of such parameters and providing a useful basis for development of an environmental exposure assessment framework. Additional parameters, and parameters describing the unique properties of polymers compared to LMW compounds, have also been suggested, many of which may be useful in higher-tier fate and exposure assessments of polymers.

Incorporation of these parameters into an environmental exposure assessment framework for polymers has been suggested in the present review based around this categorisation, highlighting which parameters may be most important both in polymer

identification and grouping, and for exposure assessment and fate modelling. However, it is clear that limitations and knowledge gaps remain; key research needs in order to develop environmental exposure assessment methodologies for polymers are identified and highlighted as follows:

- Standard identification methods for polymers which incorporate their complexity and key properties should be developed. Additionally, the relative significance of key fate parameters, particularly in polymer identification and in impacting fate behaviour, should be assessed in order to establish a base set of parameters for screening-level assessments as well as provide insight on which parameters are most significant for higher tier assessment. This will facilitate prioritisation efforts for polymers and subsequent in-depth exposure assessments.
- Research into characterising and defining polymer solidity and solubility to reduce ambiguity in classification is essential.
- The potential for polymers to further expose the environment to a complex mixture of degradation products with altered fate parameters should be accounted for in exposure assessment. In order to incorporate degradation products into a risk assessment, a deeper understanding of the pathways and products of polymer degradation under environmentally relevant conditions is required, with particular focus on potential changes in key fate parameters and environmental risk.
- There is a clear need to develop, adapt, and standardise validated and reliable analytical methods for characterisation of polymers and their degradation products, in order to measure properties relevant to exposure assessment as well as characterise degradation processes and products for exposure characterisation and

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modelling. For full characterisation, multiple techniques tailored to the polymer analyte in question may be required in tandem; for example, all of chromatography, scattering or microscopy, and spectroscopy or spectrometry may be required for complete characterisation of a non-homogeneous mixture of polymer particles. However, as knowledge of key polymer types, properties, and degradation products implicating risk assessment improves, methods can be refined and focussed to provide sufficient levels of information with minimum application of techniques.

- Whilst simple lower tier models may be appropriate for polymer exposure assessment, higher tier exposure models that account for the unique properties and fate characteristics of polymers should be developed. Adaptation of models from analysis of engineered nanoparticles may be useful for application to micro- and nano-polymer particles, such as microplastics, and a combination of modelling approaches from both LMW compounds and nanoparticles may be necessary for characterising the fate of both a solid parent polymer and its chemical degradation products. This will be further supplemented by development of QSAR approaches and datasets for polymers.
- Further research into the critical fate properties of water-soluble polymers and their breakdown products is warranted in order to better characterise their risk to the environment. This would help to prioritise data generation needs and identify polymers for further investigation.

Approaches to polymer environmental exposure and risk assessment should incorporate and allow for the complexity of polymers. Developing knowledge of how polymer properties influence fate, and therefore which are most important in characterising risk,

as well as methods to incorporate complex degradation products in exposure and hazard assessment, is essential to develop adequate and robust risk assessment methodologies for polymers.

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Figure 1: Summary of degradation and fate processes, including changes in key fate parameters, for a solid polymer material in an aquatic environment.

Figure 2: Summary of the applicability of various fate parameters and key properties to low molecular weight chemical compounds, bulk solid polymers (including particles),

and dissolved polymers. Parameters that are typically used in environmental exposure assessment of low molecular weight chemicals are further categorised in terms of basic physicochemical properties (purple), partition coefficients (red), bioconcentration and bioaccumulation (green), and biotic and abiotic degradation (light blue). Additional and polymer-specific parameters suggested in the present review, which may be useful in polymer exposure assessment, are also shown (dark blue).

Figure 3: Impact of polymer properties, analytical techniques, and fate parameters for solid and dissolved polymers in development of an environmental exposure assessment framework.

Figure 4: Size ranges of key analytical methods for analysis of polymers and polymer degradation, including the corresponding size ranges of solid polymer degradation products that can be characterised.

Table 1: Summary of key parameters used in exposure assessment of low molecular weight chemical compounds and their applicability to polymers.

Table 2: Summary of degradation data for several types of water-soluble polymers (alcohol ethoxylates, alcohol ethoxysulfates, polycarboxylates, polyethylene glycol, and polyquaterniums) obtained from a meta-review of previously collated data from the literature.

Table 3: Summary of the currently available techniques for analysis of polymer degradation in the environment.

TABLE REFERENCES

Table 2: (Federle et al. 1997; HERA 2004, 2009, 2014a, 2014b; Duis et al. 2021)

Table 3: (Cheremisinoff 1996; Witt and Röthele 1996; Jillavenkatesa et al. 2001; Moons 2002; Bootz et al. 2004; Eshel et al. 2004; Keck and Müller 2008; Michler 2008; Pyrz and Buttrey 2008; Yeo et al. 2009; Brabazon and Raffer 2010; Demuele et al. 2010; Filipe et al. 2010; Brar and Verma 2011; Rhyner 2011; Eriksen et al. 2013; Fries et al. 2013; Lambert et al. 2013a, 2013b; Deroine et al. 2014; Dümichen et al. 2014; Lee et al. 2014; Velzeboer et al. 2014; Cole and Galloway 2015; Dümichen et al. 2015; Hintersteiner et al. 2015; Löder and Gerdt 2015; Gigault et al. 2016; Lambert and Wagner 2016b, 2016a; Ter Halle et al. 2016; Balestri et al. 2017; Besseling et al. 2017; Dümichen et al. 2017; Elert et al. 2017; Frère et al. 2017; Frydkjær et al. 2017; Gigault et al. 2017; Ivleva et al. 2017; Mehn et al. 2017; Musioł et al. 2017; Nolte et al. 2017a; Primpke et al. 2017; Ter Halle et al. 2017; Araujo et al. 2018; Auta et al. 2018; Biver et al. 2018; Burns and Boxall 2018; Cabernard et al. 2018; Hermabessiere et al. 2018; Iñiguez et al. 2018; Kokalj et al. 2018; Mintenig et al. 2018; Müller et al. 2018; Oriekhova and Stoll 2018; Scheurer and Bigalke 2018; Dümichen et al. 2019; Giacomucci et al. 2019; Merzel et al. 2019; Nazareth et al. 2019)

Table 1: Summary of key parameters used in exposure assessment of low molecular weight chemical compounds and their applicability to polymers

Key parameters	Information given	Relevance to dissolved polymers?	Relevance to bulk solid polymers?	Rationalisation and comments
Basic physicochemical properties				
Water solubility	Extent of dissolution in water	Applicable	Applicable	Water solubility and dissociation constants give useful information on likely environmental compartment, and reactivity and charge distribution; both have been applied to polymers. Vapour pressure of dissolved polymers will likely be driven by LMW content (oligomers and monomers). The high molecular weights of polymers mean most will decompose before a boiling point is reached.
pK _a	Acidity (thus behaviour at environmental pH)			
T _m	Whether substance will exist as solid or liquid in environment			

P	Partitioning between air and liquid/solid phase		Not applicable	
T _b	Whether substance exists as solid/liquid or gas in environment	Not applicable		
Partition coefficients				
K _d	Partitioning between soil and water	Applicable	Not applicable	Dissolved polymers will behave similarly to LMW chemicals, meaning K _d , K _{oc} , and K _{ow} can be applied (however applicability should be assessed for those in nano-size range). Equilibrium constants are not applicable to particulate matter or colloidal solutions, for which partitioning is controlled by kinetic factors and thermodynamic equilibrium is not reached, and so application of thermodynamic parameters to bulk solid polymers is not appropriate.
K _{oc}				
K _{ow}	Partitioning between lipid (octanol) and water			
Bioconcentration and bioaccumulation				
k _u and k _d	Uptake and depuration rates	Applicable	Applicable	The concept of BCF assumes passive diffusion and is thus not relevant for polymer molecules or particles (for which active processes will play a major role in organism uptake). BAF may be applicable in some soil/sediment systems, however specific parameters for polymer accumulation should be developed and current tests should be interpreted to reflect uptake/depuration rates.
BCF	Partitioning into organisms	Not applicable	Not applicable	
BAF				
Biotic and abiotic degradation				
t _{1/2}	Time taken for concentration to reduce by half	Applicable	Applicable	Rate constants and half-lives can be applied to both dissolved and solid polymers as they provide a simple measure of degradation rate.
k _{deg}	Rate constant for (bio)degradation			

T_m = melting point; P = vapour pressure; T_b = boiling point; LMW = low molecular weight; K_d = soil/water partition coefficient; K_{oc} = soil organic carbon/water partition coefficient; K_{ow} = octanol/water partition coefficient; k_u = uptake rate constant; k_d = depuration rate constant; BCF = bioconcentration factor; BAF = bioaccumulation factor; t_{1/2} = half-life; k_{deg} = degradation rate constant

Table 2: Summary of degradation data for several types of water-soluble polymers (alcohol ethoxylates, alcohol ethoxysulfates, polycarboxylates, polyethylene glycol, and polyquaterniums) obtained from a meta-review of previously collated data from the literature.

Polymer class	Polymers covered	Methods	Results	References
Ready biodegradability				
Alcohol ethoxylates	C: 8-18 EO ^a : 2-30	OECD 301D, 301F; Closed bottle test; BOD; Sapromat	60-92 % ThOD	(HERA 2009)
	C: 10-18 EO: 3 to >20	OECD 301B; CO ₂ evolution test; Modified Sturm	60-95.4 % CO ₂ formation/ThCO ₂	
	C: 11-15 EO: 3-20	Die away screening test; modified OECD screening test	65-100 % DOC	
	C: 13 EO: 9	OECD 301E	80 % primary biodegradation	
Alcohol ethoxysulfates	C: 14-15 EO: 2.25	Modified Sturm	0.18 day ⁻¹ (mineralisation rate, CO ₂ evolution) 3.9 days (t _{1/2} , CO ₂ evolution)	(Federle et al. 1997; HERA 2004)
Polycarboxylates	P-AA, mean MW 4 kDa or not specified; P-MAA/EA, MW approx. 500 kDa; P-AM/AA, MW 10,000 kDa (25% sodium acrylate (w/w))	Modified MITI tests, closed bottle tests	<20 % biodegradation or not indicated. All polymers found to be not readily biodegradable.	(Duis et al. 2021)
Polyethylene glycol	Mean MW 0.2-57.8 kDa	OECD 301B, 310; Combined CO ₂ /DOC test	-5 to 95 % CO ₂ evolution	(Duis et al. 2021)
	Mean MW 0.2-57.8 kDa (MW _w 0.251-57.8 kDa or not specified, MW _N 0.120-25.1 kDa or not specified)	OECD 301A; Combined CO ₂ /DOC test	>70 to >90 % DOC reduction/ removal	
	Mean MW 350 Da	ISO 14593	77 % CO ₂ production (total inorganic carbon)	
	Mean MW 0.2-4,000 kDa	OECD 301B, 301E, 301F; modified OECD screening test; DIN 38412	4.1 to >95 % (endpoints not specified)	

Polyquaterniums	PQ-10, MW approx. 30,000 kDa, 1.0 meq g ⁻¹	Not specified	1 % BOD (not readily biodegradable)	(Duis et al. 2021)
	PQ-16, MW approx. 100 and 400 kDa, 2.0 and 3.0 meq g ⁻¹ (pH 7)	OECD 301F	< 10 % ThOD (mineralisation rate)	
	PG-6, MW _N > 10 kDa; PQ-10, MW _N approx. 240 kDa, MW approx. 400 kDa, 1.2 meq g ⁻¹ ; PQ-7, MW 4,300-5,200 kDa, 1.6 meq g ⁻¹	Not specified	General and ready biodegradability, qualitative data only: “not readily biodegradable”, “poorly biodegradable”	
Removal in wastewater treatment (including data for inherent biodegradability, batch, and simulation tests)				
Alcohol ethoxylates	C: 12-16 EO: 1-9	Activated sludge die away test, radiolabelled polymer	0.28-2.32 minutes (t _{1/2}) 18-146 hour ⁻¹ (k ₁)	(HERA 2009)
Alcohol ethoxysulfates	C: 12-18 EO: 2-12	SCAS and OECD CAS confirmatory test	95.4-100 % removal	(Federle et al. 1997; HERA 2004)
	C: 14-15 EO: 2.25	¹⁴ CO ₂ evolution, activated sludge system	1.79 day ⁻¹ (mineralisation rate) 0.39 days (t _{1/2})	
Polycarboxylates	P-AA (and sodium salts), mean MW 1-10 kDa; P-AA/MA (and sodium salts), mean MW 12 and 70 kDa	¹⁴ CO ₂ evolution, water (domestic activated sludge); CO ₂ production coupled with SCAS or batch activated sludge, adapted WWTP inocula	8-43 % CO ₂ evolution	(HERA 2014a, 2014b; Duis et al. 2021)
	P-AA (and sodium salts), mean MW 1-15 kDa or not specified; P-AA/MA (and sodium salts), mean MW 12 and 70 kDa; P-MAA/EA, mean MW approx. 500 kDa	OECD 302A, 302B, 303A; ISO 18749; ISO 9888, 88/302/EEC, part C	9-100 % DOC reduction	

	P-AA, mean molecular weights 1 and 2 kDa	OECD 303A	9-24 % DOC or ^{14}C removal (no clear information on test endpoint)	
	P-AA (and sodium salts), mean MW 4.5 kDa	Wastewater treatment simulation test, domestic; OECD 303A	55 and 76 % (removal of radiolabelled material)	
	P-AA, MW 4.5-215 kDa or not specified	OECD 303A; various simulation and activated sludge tests, including SCAS, CAS, treatment with FeCl_3	16-98 % overall removal	
	P-AA, mean MW 4.5 kDa	Series of batch experiments (^{14}C -labelled polymer); Primary treatment simulation	13-98 % removal	
Polyethylene glycol	Mean MW 0.2-20 kDa	OECD 302A, 303A/ISO 11733; batch system, adapted or non-adapted sludge	41-102 % DOC removal	(Duis et al. 2021)
	Mean MW 350 Da	ISO 9888 (modified)	>80 % COD reduction	
	Mean MW 1-20 kDa	CO_2 production test; various batch experiments, adapted or non-adapted sludge; OECD confirmatory test (^{14}C -labelled polymer)	40 to >90 % CO_2 evolution/mineralisation	
	Mean MW 0.3-6 kDa	OECD 302B; DIN 38412 L 24	<20 to >95 % (endpoint not specified)	
	Mean MW 4.6 kDa.	Sealed vessel test	79-86 % mineralisation (inorganic carbon production) at test end	
	Mean MW 0.6-20 kDa	Batch experiment, microorganisms from terylene plant	77-88 % primary degradation based on chemical analysis	

Polyquaterniums	PQ-7 (MW not specified).	OECD 302B	30-50 % DOC or COD elimination	(Duis et al. 2021)
	PQ-16, MW approx. 40-100 kDa, 2.0-6.1 meq g ⁻¹ (pH 7)	OECD 302B	20-70 % DOC elimination	
	PQ-6, MW _N > 10 kDa; PQ-16, MW approx. 40-400 kDa/ unspecified, 2.0-6.1 meq g ⁻¹ (pH 7)/ unspecified	OECD 302 (no further information); not specified	Qualitative data only: “not inherently biodegradable”; “Moderately/partly eliminated from water; virtually eliminated from water by e.g. sorption to activated sludge”; “Removed from waste water by e.g. strong sorption on activated sludge”	
Fate in wastewater treatment (anaerobic)				
Alcohol ethoxylates	C: 9-11 EO: 8	Measurement of gas production, digested sludge	60-83 % ThCH ₄	(HERA 2009)
	C: 9-11 EO: 8	Measurement of gas production, digested sludge	79 % ThGP	
	C: 18 EO: 7	¹⁴ CH ₄ and ¹⁴ CO ₂ evolution, digested sludge	84 % ThCH ₄ + ThCO ₂	
Polycarboxylates	P-AA/MA (and sodium salts), 70 kDa	Incubation in mixture of digester sludge and nutrient solution, radiolabelled polymer	Biodegradability extent between 11 and 16 %	(HERA 2014b)
Polyethylene glycol	Mean MW 0.4-10 kDa (included tests on mixtures of 0.4/0.6/1 kDa, and of 1.5/3/10 kDa)	Batch experiments (adapted and non-adapted digested activated sludge)	Approx. 85-92 % TOC removal	(Duis et al. 2021)
	Mean MW 0.6-20 kDa	Batch experiment, adapted micro-organisms	40-70 % primary degradation	
Degradation in river water				

Alcohol ethoxylates	C: 8-18 EO: 1-20	Rate of removal of some AE homologues, extrapolation to other chain lengths	4-24 hours (t _{1/2})	(HERA 2009)
Alcohol ethoxysulfates	C: 14-15 or not specified EO: 2.25 or not specified	¹⁴ CO ₂ evolution, river water and settled sludge supernatant; unspecified methods	0.48 day ⁻¹ and 0.7 hour ⁻¹ (mineralisation/ degradation rate). 1.4 days and approx. 1 hour (t _{1/2}). Approx. 16.6 day ⁻¹ (rate constant).	(Federle et al. 1997; HERA 2004)
Polycarboxylates	P-AA (and sodium salts), mean MW 1-10 kDa; P-AA/MA (and sodium salts), mean MW 12 and 70 kDa	¹⁴ CO ₂ evolution, river water or water and sediment, adapted or non-adapted water	6-63 % CO ₂ evolution	(HERA 2014a, 2014b; Duis et al. 2021)
Polyethylene glycol	Mean MW 0.3 kDa	River water die-away test	99 % primary biodegradation	(Duis et al. 2021)
Degradation in seawater				
Polyethylene glycol	MW _w 0.251-57.8 kDa, MW _N 0.120-25.1 kDa	Combined CO ₂ /DOC test, artificial seawater and marine micro-organisms	No biodegradation to >90 % (DOC removal)	(Duis et al. 2021)
	Mean MW 0.6 kDa	OECD 306	55 % (endpoint not specified)	
Degradation in sediment				
Polycarboxylates	P-AA (and sodium salts), mean MW 1-10 kDa; P-AA/MA (and sodium salts), mean MW 12 and 70 kDa	¹⁴ CO ₂ evolution test, sediment (river water and sediment)	6-58 % CO ₂ evolution	(HERA 2014a, 2014b)
Degradation in sediment (anaerobic)				
Alcohol ethoxylates	C: 9-11 EO: 8	Gas production, freshwater swamp material and marine sediment	66-77 % ThGP	(HERA 2009)
	C: 10-12 EO: 7.5-23	CH ₄ production, polluted creek mud	70-80 % ThCH ₄	

	C: 12 EO: 8-9	$^{14}\text{CH}_4$ and $^{14}\text{CO}_2$ evolution, pond sediment, wastewater pond sediment	13-40 % ThCH ₄ + ThCO ₂	
Polyethylene glycol	Mean MW 0.4 kDa	Anaerobic water-sediment test, marine sediments and seawater	92 % (primary degradation) 18 days ($t_{1/2}$)	(Duis et al. 2021)
Degradation in soil				
Alcohol ethoxysulfates	C: 14-15 EO: 2.25	$^{14}\text{CO}_2$ evolution, sludge-amended soil test system	0.29 day ⁻¹ (mineralisation rate) 2.4 days ($t_{1/2}$)	(Federle et al. 1997; HERA 2004)
Polycarboxylates	P-AA (and sodium salts), mean MW 1-530.4 kDa; P-AA/MA (and sodium salts), mean MW 12 and 70 kDa; P-AM/AA	$^{14}\text{CO}_2$ evolution test, sludge treated soil; biodegradation (^{13}C), agricultural soil; biodegradation (^{14}C), flask or tube reactors	0.91-35 % mineralisation/ CO_2 evolution	(HERA 2014a, 2014b; Duis et al. 2021)
	P-AM/AA, approx. 80% acrylamide and approx. 20% acrylic acid, mean MW 12,000-15,000 kDa (18% negative charge density)	Field study (8 years), agricultural site, polymer degradation (^{13}C)	13-74 % degradation relative to total amount of polymer added over 3 or 6 years 9.8% per year (mean degradation rate)	
Polyethylene glycol	Mean molecular weight 4 kDa (^{14}C labelled).	Biodegradation in three tropical soils	approx. 5-10 % mineralisation/ $^{14}\text{CO}_2$ production (read from graph)	(Duis et al. 2021)

^a Data for EO=0 (i.e. for corresponding fatty alcohols) has not been included in the present summary due to the absence of monomer units.

C = number of carbons in alcohol, EO = average number of ethoxy monomer units, ThOD = theoretical oxygen demand, ThCO₂ = theoretical carbon dioxide, DOC = dissolved organic carbon, $t_{1/2}$ = half-life, P-AA = homopolymer of acrylic acid, MW = molecular weight, P-MAA/EA = copolymer of methacrylic acid and ethyl acrylate, P-AM/AA = copolymer of acrylamide and acrylic acid, MW_w = weight average molecular weight, MW_N = number average molecular weight, BOD = biochemical oxygen demand, PQ = polyquaternium, k_1 = first order rate constant, P-AA/MA = copolymer of acrylic acid and maleic acid, WWTP = wastewater treatment plant, COD = chemical oxygen demand, PEG = polyethylene glycol, ThCH₄ = theoretical methane, ThGP = theoretical

gas production, TOC = total organic carbon, HRT = hydraulic retention time, AE = alcohol ethoxylate, LCMS = liquid chromatography mass spectrometry.

Table 3: Summary of the currently available techniques for analysis of polymer degradation in the environment

Method	Size range	Information obtained	Advantages	Limitations	References & examples of use
Mass loss	Mass based; > ca. 0.01 mg	Provides estimation of overall extent and rate of degradation, and can aid mass balance of products	<ul style="list-style-type: none"> - Fast, easy method giving overall indication of degradation - Non-destructive 	<ul style="list-style-type: none"> - Other factors besides degradation may affect mass, including oxidation, biofilm formation, and oxygen absorption - High error rates - No information on degradation pathways or products 	(Lambert et al. 2013a, 2013b; Hintersteiner et al. 2015; Ter Halle et al. 2016; Balestri et al. 2017; Auta et al. 2018)
Thermo-analytical methods (e.g. TGA, DSC)	Mass-based; 10-20 mg	Changes in thermal properties and stability	<ul style="list-style-type: none"> - Fast, simple methods giving indication of degree of degradation - Can combine with identification techniques such as FTIR and MS to provide information on thermal degradation products 	<ul style="list-style-type: none"> - Cannot confirm possible degradation pathways - Cannot obtain information on environmental degradation products 	(Cheremisinoff 1996; Deroine et al. 2014; Dümichen et al. 2014; Musioł et al. 2017)
Light microscopy	> 500 μm	Imaging of degraded macro-polymer surface, visualisation and screening of single microplastic particles	<ul style="list-style-type: none"> - Simple method for visualisation and screening - Non-destructive 	<ul style="list-style-type: none"> - Extremely high error rate for sample identification, so must couple with definitive chemical identification methods such as spectroscopy 	(Eriksen et al. 2013; Löder and Gerdt 2015; Musioł et al. 2017; Burns and Boxall 2018)
ATR-FTIR	> 500 μm	Chemical identification and changes in chemical functionality due to degradation	<ul style="list-style-type: none"> - Well-established and widely used - Fast analysis time - Non-destructive 	<ul style="list-style-type: none"> - Smaller samples may give too weak a signal - Spectral interferences from water may arise 	(Lambert and Wagner 2016b; Cabernard et al. 2018)

				- Micro-polymer particles must be visually sorted which may introduce bias	
GPC	Mass based; > ca. 20 mg	Molecular weight metrics and changes in molecular weight distribution with degradation	<ul style="list-style-type: none"> - Relatively fast and simple sample preparation - Can provide overall picture of molecular changes with degradation, as well as information on amount of polymer 	<ul style="list-style-type: none"> - High temperature required for some plastic types – potential induced degradation - Potential lower accuracy and difficulties distinguishing polymers for certain polymer types 	(Hintersteiner et al. 2015; Musiol et al. 2017; Biver et al. 2018; Müller et al. 2018; Giacomucci et al. 2019)
FPA-based micro-FTIR	> 10 μm	Simultaneous visualisation, mapping and chemical identification of polymer particles	<ul style="list-style-type: none"> - Wide area analysed, giving large numbers of spectra - No visual sorting required - Automation possible, removing bias in analysis and allowing detection of smaller particles - High resolution and non-destructive 	<ul style="list-style-type: none"> - Spectral interferences from water may arise - Time consuming - If manual not automated, particle counts may be underestimated - Environmental matrix may cause problems for detection of smaller particles 	(Ivleva et al. 2017; Primpke et al. 2017; Cabernard et al. 2018)
Raman micro-spectroscopy	> 1 μm	Simultaneous visualisation, mapping and chemical identification of polymer particles	<ul style="list-style-type: none"> - High resolution - Little interference from water - Fast, automatic data acquisition possible - Non-destructive - Higher resolution in identification compared with FTIR-based techniques 	<ul style="list-style-type: none"> - Fluorescent interferences may occur - Visual sorting often used - May require sample purification - Very time consuming - Low signal-to-noise ratio - Sample heating may damage polymer 	(Frère et al. 2017; Ivleva et al. 2017; Araujo et al. 2018; Cabernard et al. 2018; Scheurer and Bigalke 2018)
Coulter Counter	0.4 - 1200 μm	Particle concentration and	- Sensitive, consistent, high	- Spherical model may be used to	(Demuele et al. 2010; Rhyner

		size distribution	reproducibility - Large concentration range - Conductivity-based so orthogonal to optical techniques	calculate size - Particles must be suspended in electrolyte solution	2011; Lambert and Wagner 2016b; Frydkjær et al. 2017)
LD	20 nm – 3.5 mm	Particle size and size distribution	- Wide size range - Accurate and reproducible - High sensitivity - Can detect larger particles or agglomerates in a population of smaller particles, if pure LD used - Fast analysis time	- Spherical model - Inaccurate results if incorrect optical parameters used - Instruments may require additional methods and parameters for smaller particles - Possible trade-off between measurements of larger and smaller particles	(Witt and Röthele 1996; Eshel et al. 2004; Keck and Müller 2008; Lee et al. 2014; Kokalj et al. 2018)
MALS	50 – 1000 nm	Particle size	- Fast and reproducible - Can determine particle shape when coupled to other techniques such as FFF and DLS	- Matrix effects may influence results - Monodisperse samples required, therefore need coupling to separation techniques such as SEC or AF4	(Brar and Verma 2011; Gigault et al. 2017; Mehn et al. 2017; Mintenig et al. 2018)
NTA	30 - 2000 nm	Particle size and volume distributions, particle number	- Can apply to heterogeneous samples - Individual particles tracked, giving accurate sizing over broad range of distributions - Good size resolution - Some information on nature of particles from scattering intensity - Can give information on	- Spherical model - Particle concentration measurements may be imprecise - Method and sample concentration must be optimised before use - Possible instrument operation bias - Sample preparation and measurement may affect aggregation	(Filipe et al. 2010; Lambert et al. 2013a; Lambert and Wagner 2016a, 2016b)

			aggregation		
AFM	> 10 nm	Visualisation of macro-polymer surface morphology and polymer particles	<ul style="list-style-type: none"> - Can combine with IR and Raman to obtain both morphological and chemical information as well as potential subsurface information - Can obtain force-interaction curves using colloidal probe AFM - Relatively simple sample preparation and no metal coating required 	<ul style="list-style-type: none"> - Obtaining representative sample is difficult - Imaging artefacts can be problematic 	(Moons 2002; Yeo et al. 2009; Nolte et al. 2017; Iñiguez et al. 2018; Merzel et al. 2019)
DLS	3 nm – 6 μ m	Particle size and size distribution	<ul style="list-style-type: none"> - Fast and straightforward - Accurate for monodisperse suspensions - Relatively wide concentration range - Can give information on aggregation 	<ul style="list-style-type: none"> - Spherical model - Less suitable for heterogeneous samples, due to low size resolution and high sensitivity towards larger particles - Cannot determine particle concentration - Less applicable to complex or unknown samples 	(Jillavenkatesa et al. 2001; Filipe et al. 2010; Gigault et al. 2016; Besseling et al. 2017; Gigault et al. 2017; Ter Halle et al. 2017)
SEM	> 3 nm	Visualisation of polymer surface morphology, and visualisation and characterisation of polymer particle shapes and sizes	<ul style="list-style-type: none"> - High resolution - Detailed mapping and visualisation - Elemental analysis possible if coupled to EDS 	<ul style="list-style-type: none"> - Complex sample preparation which may alter nature of sample - Heavy metal staining usually required - Difficult to obtain representative sample - bias when determining size distributions of 	(Bootz et al. 2004; Brabazon and Raffer 2010; Oriekhova and Stoll 2018; Nazareth et al. 2019)

				heterogeneous particle mixtures	
TEM	> ca. 1 nm	Visualisation and characterisation of polymer particles	<ul style="list-style-type: none"> - Precise information on particle size and shape - Elemental analysis possible if coupled to EDS - Very high size resolution 	<ul style="list-style-type: none"> - Complex sample preparation which may alter nature of sample - Heavy metal staining sometimes required - Obtaining representative sample may be difficult - Thin sample required 	(Michler 2008; Pyrz and Buttrey 2008; Velzeboer et al. 2014; Cole and Galloway 2015; Gigault et al. 2016)
py-GCMS	Mass based; 3 ng – 0.5 mg	Identification of polymer type and associated additives	<ul style="list-style-type: none"> - Solvent not required, reducing background contamination - Reliable, good repeatability - Can identify complex samples such as co-polymers, polymer mixtures, polymers with additives - Spectral changes due to polymer degradation may be observable - Very low LoD for some polymers (3 ng for polystyrene) 	<ul style="list-style-type: none"> - Difficulty in analysis of plastics in complex environmental matrix - LoD depends on polymer type - Require spectral database for accurate polymer identification - Hand-picking or pre-separation of particles required - Relatively small sample sizes - Contamination or tube blocking can be an issue 	(Fries et al. 2013; Dümichen et al. 2015; Dümichen et al. 2017; Ter Halle et al. 2017; Hermabessiere et al. 2018; Mintenig et al. 2018)
TED-GCMS	Mass based; 200 ng – 100 mg	Identification of polymer type and determination of its mass fraction in an environmental sample	<ul style="list-style-type: none"> - Direct analysis of polymers in environmental matrix - Large sample sizes (up to 100 mg) and bulk 	<ul style="list-style-type: none"> - LoD depends on polymer type - Comparison to database required for identification of polymer 	(Dümichen et al. 2014; Dümichen et al. 2015; Dümichen et al. 2017; Elert et al. 2017; Dümichen et al. 2019)

			analysis allow representative sampling - High repeatability, automation possible, and can identify complex samples such as polymer blends - Low LoD for some polymers (200 ng for polystyrene) - Most contaminants do not enter GCMS system	- Matrix effects may cause issues with adsorption during the analytical process - Smaller range of compound chain lengths can be measured compared to py-GCMS	
Range of chromatography-mass spectrometry techniques	LMW chemical compounds	Characterisation and identification of chemical compounds in unknown mixtures	- Can identify compounds in complex mixtures - Robust, well-established methodology	- Often require database for comparisons of spectra and full species identification - Determination of compound structure may not be possible	(Lambert et al. 2013b)

TGA = thermogravimetric analysis; DSC = differential scanning calorimetry; FTIR = Fourier-transform infra-red; MS = mass spectrometry; ATR-FTIR = attenuated total reflection Fourier-transform infra-red; GPC = gel permeation chromatography; FPA = focal plane array; LD = laser diffraction; MALS = multi-angle light scattering; FFF = field-flow fractionation; DLS = dynamic light scattering; SEC = size-exclusion chromatography; AF4 = asymmetric flow field-flow fractionation; NTA = nanoparticle tracking analysis; AFM = atomic force microscopy; SEM = scanning electron microscopy; EDS = energy dispersive spectroscopy; TEM = transmission electron microscopy; LoD = limit of detection; py-GCMS = pyrolysis gas-chromatography mass-spectrometry; TED-GCMS = thermal extraction desorption gas-chromatography mass-spectrometry

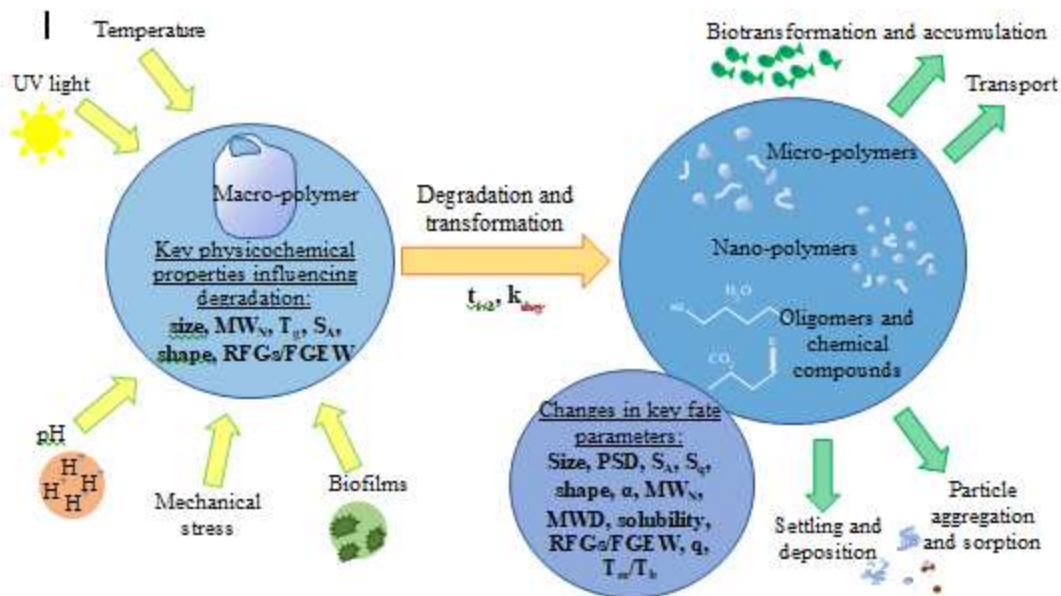


Figure 1: Summary of degradation and fate processes, including changes in key fate parameters, for a solid polymer material in an aquatic environment.

MW_N = number average molecular weight; T_g = glass transition temperature; S_A = surface area; RFG = reactive functional group; FGEW = functional group equivalent weight; $t_{1/2}$ = degradation half-life; k_{deg} = degradation rate constant; PSD = particle size distribution; S_q = surface charge; α = attachment efficiency; MWD = molecular weight distribution; q = charge or charge distribution; T_m = melting point; T_b = boiling point.

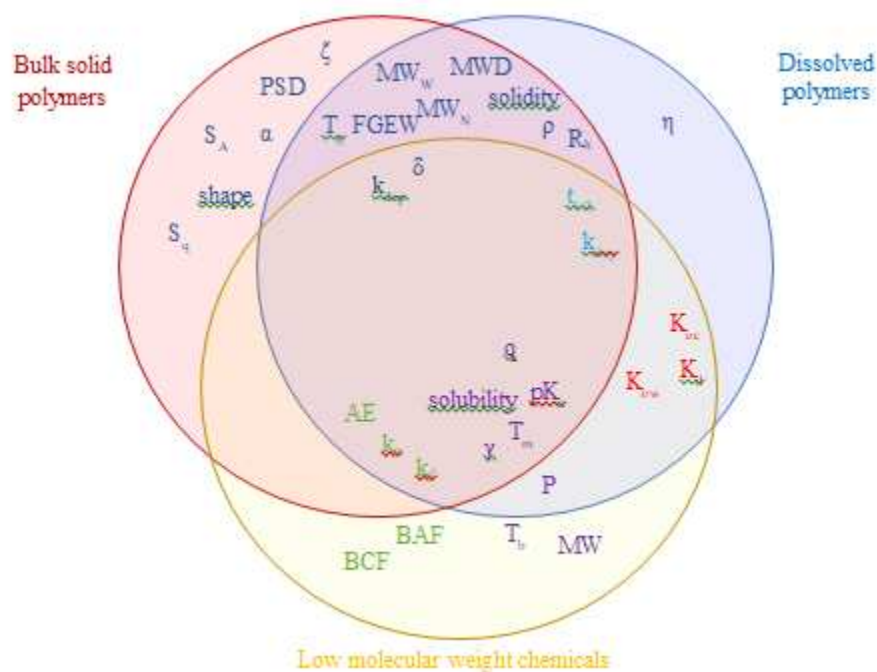


Figure 2: Summary of the applicability of various fate parameters and key properties to low molecular weight chemical compounds, bulk solid polymers (including particles), and dissolved polymers. Parameters that are typically used in environmental exposure assessment of low molecular weight chemicals are further

categorised in terms of basic physicochemical properties (purple), partition coefficients (red), bioconcentration and bioaccumulation (green), and biotic and abiotic degradation (light blue). Additional and polymer-specific parameters suggested in the present review, which may be useful in polymer exposure assessment, are also shown (dark blue).

AE = assimilation efficiency; k_{dep} = deposition rate constant; MW = molecular weight; MW_w = weight average molecular weight; R_h = hydrodynamic radius; γ = surface tension; δ = Hildebrand and Hansen solubility parameters; ζ = zeta potential; η = viscosity; ρ = density. Other abbreviations: see Figure 1 and Table 1.

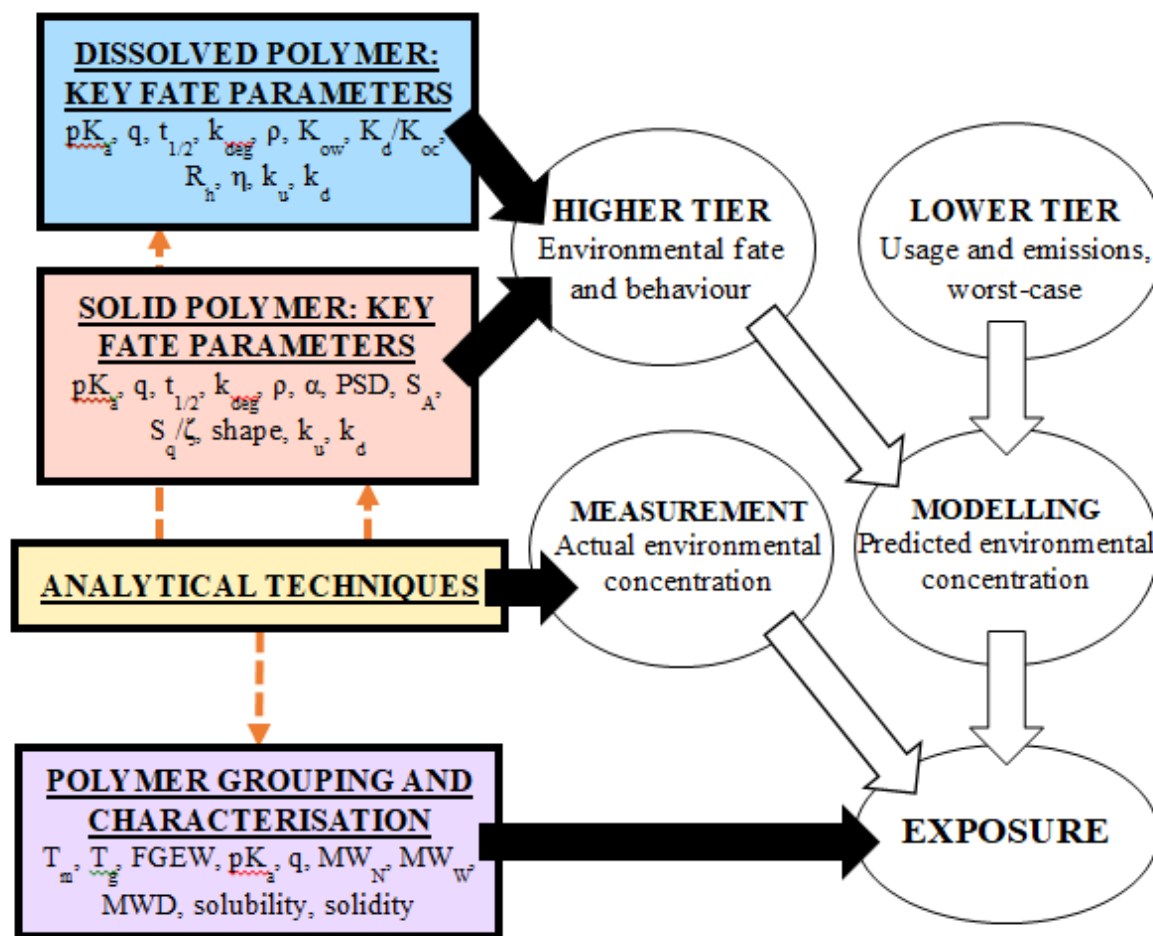


Figure 3: Impact of polymer properties, analytical techniques, and fate parameters for solid and dissolved polymers in development of an environmental exposure assessment framework.

Abbreviations: see Figures 1-2 and Table 1.

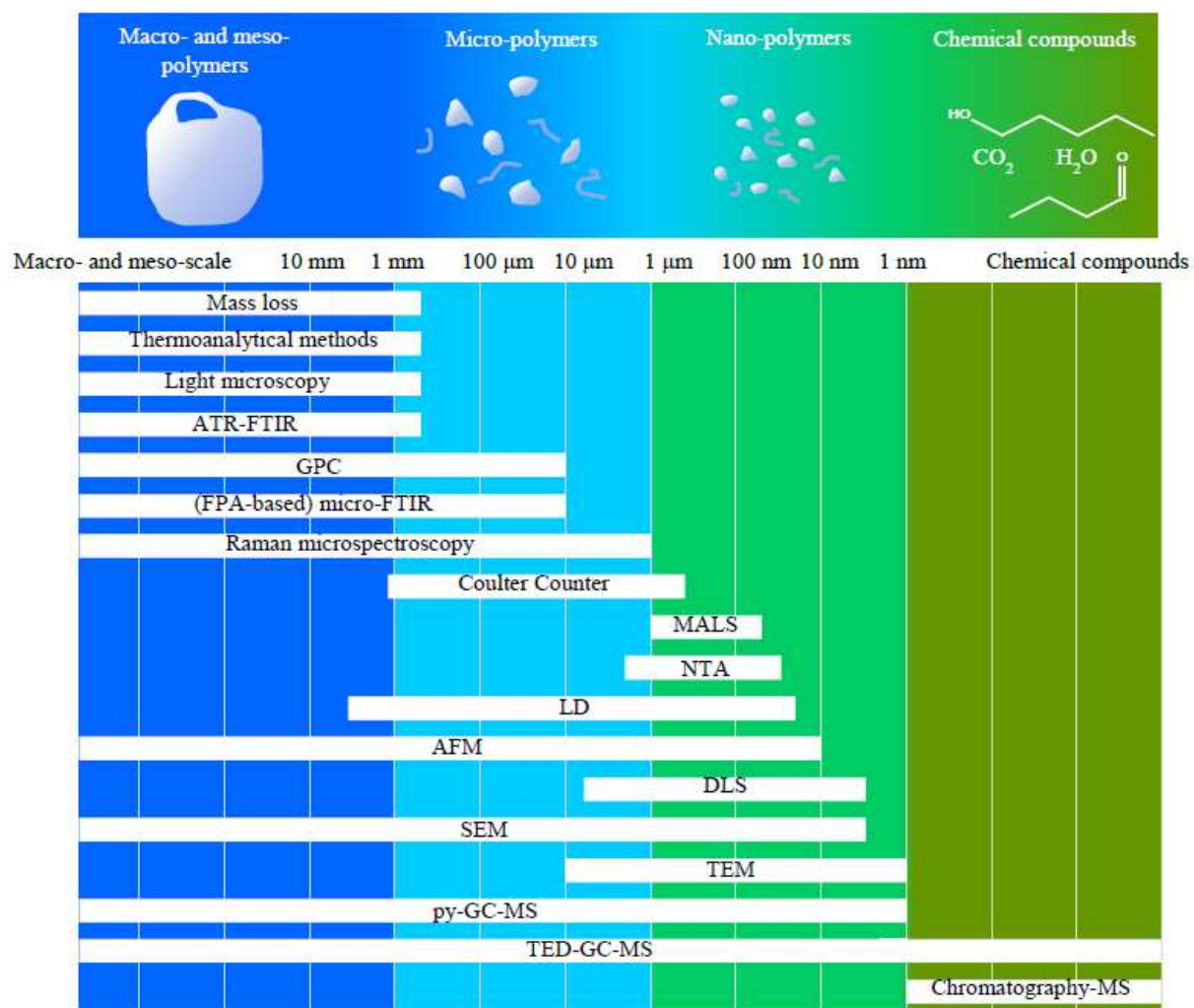


Figure 4: Size ranges of key analytical methods for analysis of polymers and polymer degradation, including the corresponding size ranges of solid polymer degradation products that can be characterised. Abbreviations: see Table 2.