Critical Review

Toward a Framework for Environmental Fate and Exposure Assessment of Polymers

Hattie Brunning,a,* J. Brett Sallach,a Victor Zanchi,b Oliver Price,b and Alistair Boxall,a,*

aDepartment of Environment and Geography, University of York, York, United Kingdom
bReckitt Benckiser, Hull, United Kingdom

Abstract: Development of risk-assessment methodologies for polymers is an emerging regulatory priority to prevent negative environmental impacts; however, the diversity and complexity of polymers require 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 nonpolymeric 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 limitations and knowledge gaps are then identified and discussed, specifically the complexity of polymer identification, with the need for characterization of the most significant parameters for polymer grouping and prioritization; 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 standardization of analytical methods for characterization of polymer fate properties and degradation products; and the need to develop exposure modeling approaches for polymers. Environ Toxicol Chem 2022;41:515–540. © 2021 The Authors. Environmental Toxicology and Chemistry published by Wiley Periodicals LLC on behalf of SETAC.

Keywords: Ecological risk assessment; Environmental fate; Microplastics; Contaminants of emerging concern; Environmental exposure assessment; Nanoplastics

INTRODUCTION

The prevalence and persistence of polymers in the environment have resulted in heightened concern in public, scientific, and regulatory communities. Polymers have previously been subjected to reduced regulatory requirements compared to low–molecular weight (LMW) chemicals, for example, under the European Union regulation Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH; European Commission, 2006); and there increasingly have 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 because of their widespread release into, and persistence in, the environment (Burns & Boxall, 2018; Derraik, 2002; Ileva et al., 2017; Koelmans et al., 2017; Thompson et al., 2009), with a number of risk-assessment strategies being suggested for microplastics (Gouin et al., 2019; Hüffer et al., 2017; Syberg et al., 2015). 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 (see Arp & Knutsen, 2020; Xiong, Loss, et al., 2018). 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 & Knutsen, 2020); and it is inevitable that they will be...
released to the environment. In addition, 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 modeling (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 characterization 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 to evaluate and mitigate the potential environmental impacts of polymers. In the present review, environmental exposure assessment of polymers will be discussed in the context of their applicability to polymers. Moreover, the analytical methods to determine concentrations and properties of LMW chemicals in fate studies may be insufficient for characterization 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 to evaluate and mitigate the 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 as follows:

1) Briefly discuss current approaches to prospective environmental risk assessment (ERA) 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 modeling.
4) Identify priorities and future research needs based on these considerations.

**CURRENT APPROACHES TO ENVIRONMENTAL EXPOSURE ASSESSMENT**

Exposure assessment is key in ERA, with exposure predictions being combined with ecotoxicity data to determine risk, often by calculation of a risk quotient using the predicted-environmental concentration and the predicted-no-effect concentration (Amiard & 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 (BCFs and BAFs, respectively), and biotic and abiotic degradation rates, with standard Organisation for Economic Co-operation and Development (OECD) test methods for their measurement.

Because experimental fate and property data are sometimes only available for a small proportion of chemical substances in use, structure–activity relationships and quantitative structure–activity relationships (QSARs) are often utilized where the data are insufficient or unavailable. Models of QSARs such as those in EPI Suite have been established for prediction of physicochemical properties (e.g., water solubility, vapor pressure, Henry's law constant, and octanol–water partition coefficient [KOW]) and environmental fate parameters (e.g., degradation half-lives and sorption coefficients) of chemicals (US Environmental Protection Agency [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 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); the European Union system for the evaluation of substances (Vermeire et al., 1997), which may be used to quantify exposure and risk of chemicals (e.g., under REACH); and the Forum for the Co-Ordination of Pesticide Fate Models and Their Use (FOCUS) models for estimating concentrations of plant protection products (FOCUS Working Group on Surface Water Scenarios, 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 characterize 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 modeling 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 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 (MWs) 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 (MWN and MWW, respectively) and molecular weight distribution (MWD). Polymers have widespread usage and are released to the environment in both solid form (e.g., plastics [Kawecki & Nowack, 2019]) and dissolved form (e.g., from water treatment and agriculture [Arp & 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 MW distribution for each MWN, polymers of a wide range of MWW 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 Chemical Abstracts Service (CAS) numbers (which are based on incorporated monomers) are insufficient to differentiate polymers because the same name and CAS number may apply to two polymers with vastly different properties. In addition, 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 nanoscale particles, oligomers, and LMW chemical compounds (see Lambert et al., 2013a, 2013b; Saad et al., 2010; 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 “macropolymer,” “mesopolymer,” “micropolymer,” and “nanopolymer” 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 these data for many current-use polymers may limit characterization of exposure (Duis et al., 2021). However, for more complex, higher-tier environmental exposure-assessment studies which incorporate data on fate behavior, 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 (see Cumming, 2008; DeLeo et al., 2020; HERA, 2004, 2009, 2014a, 2014b), 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 MWs.

A primary concern for higher-tier environmental exposure assessment is the establishment of key parameters to measure the behavior 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 modeling. The applicability of established fate parameters for LMW chemical compounds to polymers is first discussed and summarized in Table 1. We suggest that both homo- and copolymers can be grouped either as solid polymers (including bulk macroscopic solids and particles) or as 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 the applicability of both established fate parameters and suggested polymer-specific parameters. This grouping underpins the following discussion.

### Basic physicochemical properties

Boiling points are typically not relevant for most polymers because, by definition, polymers exist as macromolecules with HMWs and typically decompose before boiling (see Schupp et al., 2018). Similarly, vapor pressure (P) will generally remain low for dissolved polymers because of their HMW. While vapor pressure can be measured for some liquid polymers, it is likely that it is LMW and oligomeric components that contribute most to P (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 (Risk & Policy Analysts, GnoSys, & Milieu, 2012).

Conversely, melting points (Tm) are applicable to both LMW and HMW polymers. In the context of polymers, the Tm refers to the transition between crystalline and amorphous states and applies only to semicrystalline polymers (Alsenbein & 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 (Fukushima et al., 2013; Khatiwala et al., 2008).

Reactive functional groups (RFGs) also influence environmental fate, and in contrast to LMW chemical compounds, the functional group equivalent weight is important for polymers because it describes the relative proportion of RFGs within the polymer (ECETOC, 2019). Anionic and cationic polymers are analogous to acidic and basic polymers, respectively.
### 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? | Rationalization 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. Vapor 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. |
| pKₐ                             | Acidity (thus behavior at environmental pH)                                       | Applicable                        | Applicable                        |                                                                                               |
| Tₘ                              | Whether substance will exist as solid or liquid in environment                    | Applicable                        | Applicable                        |                                                                                               |
| P                               | Partitioning between air and liquid/solid phase                                  | Applicable                        | Not applicable                    |                                                                                               |
| Tₒ                              | Whether substance exists as solid/liquid or gas in environment                    | Not applicable                    | Not applicable                    |                                                                                               |
| **Partition coefficients**       |                                                                                   |                                  |                                   |                                                                                               |
| Kₒ                              | Partitioning between soil and water                                              | Applicable                        | Not applicable                    | Dissolved polymers will behave similarly to LMW chemicals, meaning Kₒ, KₒC, and KₒW can be applied (however, applicability should be assessed for those in the 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, so application of thermodynamic parameters to bulk solid polymers is not appropriate. |
| KₒC                             | Partitioning between lipid (octanol) and water                                   | Applicable                        | Not applicable                    |                                                                                               |
| KₒW                             | Partitioning between lipid (octanol) and water                                   | Applicable                        | Not applicable                    |                                                                                               |
| **Bioconcentration and bioaccumulation** |                                                                                   |                                  |                                   |                                                                                               |
| kᵤ and k₅                       | 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). In some soil/sediment systems, BAF may be applicable; 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                             | Partitioning into organisms                                                      | Not applicable                    | Not applicable                    |                                                                                               |
| **Biotic and abiotic degradation** |                                                                                   |                                  |                                   |                                                                                               |
| t₁/₂                            | Time taken for concentration to reduce by half                                    | Applicable                        | Applicable                        | Rate constants and half-lives can be applied to both dissolved and solid polymers because they provide a simple measure of degradation rate. |
| kᵩᵣᵩ                             | Rate constant for (bio)degradation                                                 | Applicable                        | Applicable                        |                                                                                               |

pKₐ = dissociation constant; Tₘ = melting point; P = vapor pressure; Tₒ = boiling point; Kₒ = soil–water partition coefficient; KₒC = soil organic carbon–water partition coefficient; KₒW = octanol–water partition coefficient; kᵤ = uptake rate constant; k₅ = depuration rate constant; BCF = bioconcentration factor; BAF = bioaccumulation factor; t₁/₂ = half-life; kᵩᵩ = degradation rate constant; LMW = low molecular weight.
(see Guiney et al., 1998; Hennecke et al., 2018; Ostolska & Wiśniewska, 2014), and measurement of their dissociation constants can enable prediction of their charge or charge distribution at environmental pH (see 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 (see Cumming et al., 2008; Costa et al., 2014; Goodrich et al., 1991; USEPA, 1997). Charge also influences environmental fate processes such as sorption (Blachier et al., 2009; Galvão et al., 2007). Surface tension (γ) is relevant for dissolved and colloidal polymers with surfactant properties, with surfactant behavior being recognized as significant for environmental fate and effects (see Jardak et al., 2016).

Partition coefficients

Parameters such as the soil–water and soil organic carbon–water partition coefficients (K₇ and K₀C, respectively [Kookana et al., 2014]) are used to assess the partitioning of chemicals between soil/sediment/sludge and water (Amiard & Amiard-Triquet, 2015) and are useful in predicting the concentrations of a chemical in these environmental compartments. Although terrestrial environments and soils are important receiving compartments of both solid and dissolved polymers (because of application of, e.g., sludge, mulch, agrochemicals, and soil conditioners [Arp & Knutsen, 2020; Felsot et al., 2011; Horton et al., 2017]), the use of K₇ and K₀C 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 dependent on time, concentration, and system conditions (Kookana et al., 2014; Praetorius et al., 2014). It therefore follows that application of K₀C and K₇, as well as other commonly used equilibrium-based partition coefficients such as K₇W, 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 (see Min et al., 2020).

These parameters may therefore be applied to dissolved polymers because these will follow equilibrium partitioning behavior. Equilibrium partition coefficients have been previously applied to polymer macromolecules (Gorbunov & Skvortsov, 1995; Lazzara & Deen, 2004; Tong & Anderson, 1996; White & Deen, 2000), usually in the context of partitioning between a gel and solution but also in an environmental context, albeit rarely (Cumming et al., 2011a, 2011b). However, use of K₇W to indicate potential for bioaccumulation may be insufficient for HMW polymers because of uptake by nonpartitioning processes (see section Bioconcentration and Bioaccumulation). Given that polymer molecules in solution can also exist in the nano-size range (Armstrong et al., 2004; Arp & Knutsen, 2020; Xiong, Miller, et al., 2018), 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 the 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

Often, BCFs and BAFs are used in fate and hazard assessments of chemicals (see Berrojalbiz et al., 2009; Castro et al., 2019; J.-P. Wu et al., 2011) to characterize uptake and accumulation into organisms in the environment. While the BCF accounts for uptake of a chemical substance only via dermal and respiratory absorption, the BAF accounts for additional uptake via ingestion (Amot & Gobas, 2006; Mackay et al., 2013). Because the concept of BCF assumes passive diffusion, it is known to be inapplicable to nanoparticles (Kookana et al., 2014; Kühnel & Nickel, 2014) because equilibrium partitioning does not apply and active processes such as endocytosis play a significant role in nanoparticle uptake because of 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 internalization rates and attachment efficiencies (α) should be identified and developed for nanoparticle bioaccumulation (Kühnel & 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/desorption rates rather than BCFs (Kookana et al., 2014); uptake and depuration rate constants, as well as assimilation efficiency, have been applied to nanoparticles previously (Dai et al., 2015; Zhao & Wang, 2010).

Knowledge from medicinal chemistry shows that endocytosis also plays a role in cell uptake of polymer molecules (Apostolovic et al., 2011) because of 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 (Fröhlich, 2012; Liechty et al., 2010). These properties may therefore be important for characterization of biological fate processes of both solid and dissolved polymers.

Abiotic and biotic degradation

Degradation rates have been often assessed for polymers (see Auta et al., 2018; Gómez & Michel, 2013; Hennecke et al., 2018; Lambert et al., 2013a), and the degradation parameters half-life
and degradation rate constant ($t_{1/2}$ and $k_{\text{deg}}$, respectively) remain applicable; however, the increased complexity of polymer degradation mechanisms and products should also be considered. While degradation products of LMW chemicals are routinely incorporated into ERAs, 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 (see Lambert et al., 2013a, 2013b; Saad et al., 2010; Ter Halle et al., 2016; Weinstein et al., 2016). The complexity of the product mixture from degradation of a solid polymer along with the implications for polymer properties and key fate parameters are illustrated in Figure 1.

Degradation mechanisms and $t_{1/2}$ and $k_{\text{deg}}$ values depend on both polymer properties (including the presence of certain RFGs, hydrophobicity, MW, glass transition temperature ($T_g$), and fragment size, among others [Min et al., 2020; Ter Halle et al., 2017]) and environmental factors (including light and oxygen availability, temperature, pH, salinity, and biofilm formation [Da Costa et al., 2018; Lambert et al., 2013a; 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 characterizing potential risk. Standard test methods will require modification and additional analytical techniques to characterize these products and corresponding degradation pathways.

Polymer particles may be formed from breakdown of a solid polymer; in addition, while 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 & Knutsen, 2020); and it should be noted that polymer solubility does not preclude nonbiodegradability and environmental persistence (Arp & Knutsen, 2020; Hennecke et al., 2018; Swift, 1998). 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 (see Frydkjær et al., 2017), and both primary and secondary particles which have been exposed to the environment may have altered density (Chubarenko et al., 2016; Morét-Ferguson et al., 2010) and surface properties (Waldman & Rillig, 2020), with different RFGs, charge ($S_A$), and topography (Fotopoulou & Karapanagioti, 2012). These changes will influence fate; for example, the surfaces of ultraviolet light-degraded polystyrene nanoparticles have been shown to be more oxygen-rich, potentially influencing aggregation behavior, compared to nondegraded 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 prioritization methodologies classify polymers of high average MW ($\geq 1000$ Da) as low concern (PLC) because of 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 that have been discussed and that are summarized 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 summarized 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 $MW_D$. The presence of leachable LMW compounds or oligomers in a polymer is also important because these may be more bioavailable (see Bejgarn et al., 2015). The $MW_N$, $MW_W$, $MW_D$, and LMW content of polymers can be characterized using size exclusion chromatography (OECD, 1996a, 1996b).

An important property determining fate is solubility. Hildebrand and Hansen solubility parameters ($\delta$; Miller-Chou & 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 (Hartmann et al., 2019; OECD, 2000). Polymer solubility is also key for their classification within the framework of the present review, along with polymer solubility or hardness; solubility is also significant for the ECHA definition of microplastics as solid (ECHA, 2019) and may influence environmental fate (e.g., by influencing biofilm formation [Muthukumar et al., 2011]). Solid polymers also have several properties which are not shared with dissolved polymers but 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 ($\rho$) 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 modeling study, Besseling et al. (2017) found that while 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 nanoparticle on the sea surface, suggesting that smaller debris may have different flotation behavior 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 fibers (OECD, 1981). While 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 may be important in characterizing their fate. As well as influencing transport and vertical distribution, particle size may 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 $S_m$ may be important (see Fotopoulou & Karapanagioti, 2012). Surface charge of nano-scale polymer particles in colloidal suspensions can be assessed by measurement of the zeta potential ($\xi$), which influences stability and therefore aggregation behavior (Cai et al., 2018; Liu et al., 2019; Oriekhova & Stoll, 2018; Saavedra et al., 2019; J. 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

![FIGURE 2: Summary of the applicability of various fate parameters and key properties to low–molecular weight (LMW) chemical compounds, bulk solid polymers (including particles), and dissolved polymers. Parameters that are typically used in environmental exposure assessment of LMW chemicals are further categorized in terms of basic physicochemical properties (purple), partition coefficients (red), bio-concentration 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). $\xi$ = zeta potential; PSD = particle size distribution; $MW_W$ = weight average molecular weight; $MW_D$ = molecular weight distribution; $S_A$ = surface area; $\alpha$ = attachment efficiency; $\gamma$ = glass transition temperature; $FGEW$ = functional group equivalent weight; $MW_N$ = number average molecular weight; $\rho$ = density; $R_h$ = hydrodynamic radius; $\eta$ = viscosity; $\text{k}_{\text{dep}}$ = deposition rate constant; $\delta$ = Hildebrand and Hansen solubility parameters; $S_m$ = surface charge; $\text{k}_{\text{deg}}$ = degradation half-life; $\text{k}_{\text{bio}}$ = bioaccumulation factor; $\text{BCF}$ = bioconcentration factor; $T_b$ = boiling point; $MW$ = molecular weight.](wileyonlinelibrary.com/ETC)
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 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 ranges (Bergmann et al., 2019; Kawecki & Nowack, 2019; Wright et al., 2020) and dissolved polymers present in aerosols, for example, in agricultural sprays (see 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 & Soares, 1995), may be important for liquid polymers. In addition to Tm, T0 is useful in polymer matrix characterization because 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; while mass concentration remains sufficient for dissolved polymers, for solid polymers and particles, number concentration and 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 (Schwaferts et al., 2019; Ter Halle et al., 2016), meaning the metric measured may influence conclusions drawn about relative environmental impacts.

**Analytical techniques for polymer characterization**

It has been recognized that standard test methods may need to be adapted for application to polymers (ECETOC, 2020). While 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 characterization of a polymer. The traditional methodologies used for chemical analysis, including chromatography and mass spectrometry, may need to be adapted or replaced to characterize parameters such as shape, aggregation behavior, and topography. In addition, the existence of a “methodological gap” in the nano-size range has been highlighted (Schwaferts et al., 2019), and it has been recognized multiple times in the literature that there is a lack of both standardization and adequate validation of some techniques for plastic particle analysis (Burns & Boxall, 2018; Hidalgo-Ruz et al., 2012; Ivleva et al., 2017; Pico et al., 2019). Knowledge from nanoparticle and microplastic analyses 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 characterized. Fully characterizing 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 ERA.

**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, MW, and macromolecular properties. A lack of data on polymer environmental fate will also limit development of polymer QSARs. Although models such as the Ecological Structure–Activity Relationship model 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, Peijnenburg, et al., 2017).

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. While 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 that we have described. For example, models such as the FOCUS models for pesticides (FOCUS Working Group on Surface Water Scenarios, 2001) and the exposure to Pharmaceuticals in the Environment (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 because 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, MW, and macromolecular properties such as chain conformation are likely to influence dissolved polymer fate.

**TOWARD A FRAMEWORK FOR POLYMER EXPOSURE ASSESSMENT**

To move toward 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 characterization of polymers, which can also facilitate polymer grouping and prioritization. Approaches to polymer grouping have been discussed in detail by ECETOC (2019); in the present review we highlight key parameters for polymer characterization for exposure assessment based on the discussion of fate parameters, including properties such as MW parameters, solubility, presence of functional groups, and transition temperatures.

We have also identified the most relevant parameters for higher-tier exposure modeling (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 ERA because 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. While parameters such as $k_{\text{deg}}$, $T_{1/2}$, 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 characterization of key parameters for polymers.

From this framework (Figure 3), key considerations to address knowledge gaps can be identified, including the most important parameters for polymer identification, grouping, prioritization, and fate analysis; complex degradation processes and by-products of polymers; available analytical techniques for polymer analysis; and fate and exposure modeling of polymers. These considerations are addressed in the context of the exposure-assessment framework (Figure 3) in the following section.

**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 summarized 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 MW (MW$_N$, MW$_W$, and 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 behavior. Development of grouping approaches based on correlation between key parameters and environmental behavior 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 behavior of polymers is likely to be achieved through a combination of experimental fate studies and modeling; 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 modeling, 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 behavior (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 prioritization 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 cutoff points for solubility 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 LMW, parameters that would normally only be relevant for LMW chemical substances and oligomers (such as P and BCF) may become relevant, so it may be important to define MW cutoff points for such parameters. In addition, as knowledge develops of which properties of particles may confer hazard, such as shape and surface properties (see Della Torre et al., 2014; Frydkjær et al., 2017), the relative importance of these parameters for grouping of micro- and nanoplastics 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, simulation tests which closely mimic environmental conditions (e.g., OECD, 2004b), to study net degradation processes and products, are likely to be more useful in characterizing 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 copolymers as part of the HERA project (HERA, 2004, 2009, 2014a, 2014b), with degradation data for these classes of polymers being summarized 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 summarized the aforementioned collated degradation data for these polymer types, 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 focused 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 nonstandard methods.

While 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 few data available for polyquaterniums as a class (DUIS et al., 2021), despite potential concerns relating to the environmental hazard of cationic polymers (see USEPA, 1997). In addition, a lack 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 standardization 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 summarized together in the present review. Importantly, many studies focus on the extent of degradation and associated biodegradability endpoints (Table 2), whereas full environmental exposure assessment will in many cases require treatment of the degradation products formed. In addition, tests focused 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 mineralization; 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 characterize 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 characterized, which product types are most significant in terms of environmental risk, and how polymer properties can be predictive of degradation products (see Min et al., 2020) is warranted.

**Characterization of polymers and degradation products**

A further key consideration for polymer exposure assessment is the analytical tools available to characterize 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
### 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*: 2–30 | OECD 301D, 301F; closed bottle test; BOD; Sapromat | 60%–92% ThOD | Human & Environmental Risk Assessment on Ingredients of European Household Cleaning Products (HERA, 2009) |
|                               | C: 10–18, EO: 3 to >20 | OECD 301B; CO₂ evolution test; modified Sturm | 60%–95.4% CO₂ formation/ThCO₂ |            |
|                               | 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 (mineralization rate, CO₂ evolution) | Federle et al. (1997), HERA (2004) |
| Polycarboxylates              | P-AA, mean MW 4 kDa or not specified; P-MAA/EA, MW -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 CO₂/DOC test | -5% to 95% CO₂ 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 CO₂/DOC test | >70% to >90% DOC reduction/removal |            |
|                               | Mean MW 350 Da | ISO 14593 | 77% CO₂ production (total inorganic carbon) |            |
|                               | Mean MW 0.2–4000 kDa | OECD 301B, 301E, 301F; modified OECD screening test; DIN 38412 | 4.1% to >95% (endpoints not specified) |            |
| Polyquaterniums               | PQ-10, MW -30,000 kDa, 1.0 meq g⁻¹ | Not specified | 1% BOD (not readily biodegradable) | Duis et al. (2021) |
|                               | PQ-16, MW -100 and 400 kDa, 2.0 and 3.0 meq g⁻¹ (pH 7) | OECD 301F | <10% ThOD (mineralization rate) |            |
|                               | PG-6, MW_N > 10 kDa; PQ-10, MW_N -240 kDa, MW -400 kDa, 1.2 meq g⁻¹; PQ-7, MW 4300–5200 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, radiolabeled polymer | 0.28–2.32 min (t_{1/2}) | HERA (2009) |
|                               |                  |         | 18–146 h⁻¹ (k_i) |            |
| 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 | ¹⁴CO₂ evolution, activated sludge system | 1.79 day⁻¹ (mineralization rate) |            |
|                               |                  |         | 0.39 days (t_{1/2}) |            |

(Continued)
| Polymer class      | Polymers covered                                                                 | Methods                                                                 | Results                              | References                                      |
|--------------------|---------------------------------------------------------------------------------|-------------------------------------------------------------------------|--------------------------------------|------------------------------------------------|
| Polycarboxylates   | P-AA (and sodium salts), mean MW 1–10 kDa; P-MAA (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              | Duis et al. (2021), HERA (2014a, 2014b)        |
|                    | 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 ~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                                        | Wastewater treatment simulation test, domestic; OECD 303A               | 55% and 76% (removal of radiolabeled 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-labeled polymer); primary treatment simulation | 13%–98% removal                      |                                                 |
| Polyethylene glycol| Mean MW 0.2–20 kDa                                                             | OECD 302A, 303A/ISO 11733; batch system, adapted or nonadapted 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 nonadapted sludge; OECD confirmatory test ($^{14}$C-labeled polymer) | 40% to >90% CO$_2$ evolution/mineralization |                                                 |
|                    | 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% mineralization (inorganic carbon production) at test end |                                                 |
|                    | Mean MW 0.6–20 kDa                                                             | Batch experiment, microorganisms from butylene plant                     | 77%–88% primary degradation based on chemical analysis |                                                 |
| Polyquaterniums    | PQ-7 (MW not specified), PQ-16, MW 40–100 kDa, 2.0–6.1 meq g$^{-1}$ (pH 7)    | OECD 302B                                                                | 30%–50% DOC or COD elimination     | Duis et al. (2021)                               |
|                    | PQ-6, MW >10 kDa; PQ-16, MW 4–400 kDa/unspecified, 2.0–6.1 meq g$^{-1}$ (pH 7)/unspecified | OECD 302B (no further information); not specified                      | 20%–70% DOC elimination            |                                                 |

Qualitative data only: “not inherently biodegradable”; “moderately/partly eliminated from water; virtually eliminated from water by, e.g., sorption on activated sludge”; “removed from waste water by, e.g., strong sorption on activated sludge”
| Polymer class | Polymers covered | Methods | Results | References |
|---------------|------------------|---------|---------|------------|
| Fate in wastewater treatment (anaerobic) | Alcohol ethoxylates | C: 9–11, EO: 8 | Measurement of gas production, digested sludge | 60%–83% ThCH₄ | HERA (2009) |
| | | C: 9–11, EO: 8 | | 79% ThGP | |
| | | C: 18, EO: 7 | | 84% ThCH₄ + ThCO₂ | |
| | Polycarboxylates | P-AA/MA (and sodium salts), 70 kDa | Incubation in mixture of digested sludge and nutrient solution, radiolabeled 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 nonadapted digested activated sludge) | ~85%–92% TOC removal | Duis et al. (2021) |
| | | Mean MW 0.6–20 kDa | | 40%–70% primary degradation | |
| Degradation in river water | Alcohol ethoxylates | C: 8–18, EO: 1–20 | Rate of removal of some alcohol ethoxylate homologs, extrapolation to other chain lengths | 4–24 h (t₁/₂) | HERA (2009) |
| | Alcohol ethoxysulfates | C: 14–15 or not specified EO: 2.25 or not specified | ¹⁴CO₂ evolution, river water and settled sludge supernatant; unspecified methods | 0.48 day⁻¹ and 0.7 h⁻¹ (mineralization/degradation rate) | Federle et al. (1997), HERA (2004) |
| | | | 1.4 days and ~1 h (t₁/₂) | | |
| | | | | | |
| | Polycarboxylates | P-AA (and sodium salts), mean MW 1–10 kDa; P-AA/MA (and sodium salts), mean MW 12 and 70 kDa | ¹⁴CO₂ evolution, river water or water and sediment, adapted or nonadapted water | 6%–63% CO₂ evolution | Duis et al. (2021), HERA (2014a, 2014b) |
| | Polyethylene glycol | Mean MW 0.3 kDa | River water die-away test | 99% primary biodegradation | Duis et al. (2021) |
| Degradation in seawater | Polyethylene glycol | MWᵥ 0.251–57.8 kDa, MWₜ 0.120–25.1 kDa | Combined CO₂/DOC test, artificial seawater and marine microorganisms OECD 306 | No biodegradation to >90% (DOC removal) | Duis et al. (2021) |
| 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 | ¹⁴CO₂ evolution test, sediment (river water and sediment) | 6%–58% CO₂ 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 | CH₄ production, polluted creek mud | 70%–80% ThCH₄ | |
| | | C: 12, EO: 8–9 | ¹⁴CH₄ and ¹⁴CO₂ evolution, pond sediment, wastewater pond sediment | 13%–40% ThCH₄ + ThCO₂ | |
| | Polyethylene glycol | Mean MW 0.4 kDa | Anaerobic water–sediment test, marine sediments and seawater | 92% (primary degradation) 18 days (t₁/₂) | |
| Degradation in soil | Alcohol ethoxysulfates | C: 14–15, EO: 2.25 | ¹⁴CO₂ evolution, sludge-amended soil test system | 0.29 day⁻¹ (mineralization rate) 2.4 days (t₁/₂) | Federle et al. (1997), HERA (2004) |
we present a holistic overview of how analytical tools could be deployed and further developed to better characterize 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 nanoplastics from soils, sediments, and biota, including density separation and chemical or enzymatic digestion (see Hurley et al., 2018; Karlsson et al., 2017). However, these treatments may alter the particle analytes (Enders et al., 2017; Hurley et al., 2018; Rist et al., 2017), 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 (see Basheer et al., 2005; Berloz-Barbier et al., 2014; Martínez-Parreño et al., 2008), which may be developed and optimized for dissolved polymers (see Pantini et al., 2011).

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

Microscopy, particularly light microscopy and scanning electron microscopy, is commonly used in visualization of plastics, allowing characterization of size and shape of particles (see Hernandez et al., 2017; Oriekhova & Stoll, 2018; Ter Halle et al., 2016) and surface degradation of macromolecules (Gómez & Michel, 2013; Musiol et al., 2017). However, unequivocal chemical identification of the analyte is essential and relies on combination with spectroscopic methods such as Fourier-transform infrared (FTIR) and Raman spectroscopy (Burns & 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–based micro-FTIR (Löder et al., 2015; Pimpke 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 (see Gigault et al., 2016; Lambert & Wagner, 2016a; Mintenig et al., 2018). Laser diffraction instruments in particular have the potential to cover a wide particle size range (Keck & Müller, 2008; Witt & Röthele, 1996), and dynamic light scattering (DLS) and nanoparticle tracking analysis are useful for characterizing particle aggregation (see Besseling et al., 2017; Filipe et al., 2010; Gigault et al., 2017). However, such techniques typically utilize spherical models to describe particles (see Eshel et al., 2004; Frydkjær et al., 2017; Lambert & Wagner, 2016b), which may influence analysis of irregularly shaped secondary particles. Techniques such as DLS and multi-angle light scattering (MALS) may also require repreparation of particles into specific size fractions, which can be achieved using asymmetric flow field-fractionation (AF4; see Filipe et al., 2010; Gigault

### Table 2: (Continued)

| Polymer class | Polymers covered | Methods | Results | References |
|---------------|------------------|---------|---------|------------|
| **Polyacrylates** | P-AM (e.g., sodium salts), mean MW 4,400 kDa; P-AM/AA (and sodium salts), mean MW 12 and 70 kDa; P-AAM/AA | 13%–19% mineralization/CO₂ evolution | Duis et al. (2021), HERA (2014) | |
| Method                          | Size range         | Information obtained                                                                 | Advantages                                                                 | Limitations                                                                 | References and examples of use                                                                 |
|--------------------------------|--------------------|----------------------------------------------------------------------------------------|----------------------------------------------------------------------------|----------------------------------------------------------------------------|---------------------------------------------------------------------------------------------|
| Mass loss                      | Mass-based; >~0.01 mg | Provides estimation of overall extent and rate of degradation and can aid mass balance of products | - Fast, easy method giving overall indication of degradation  
- Nondestructive | - Other factors besides degradation may affect mass, including oxidation, biofilm formation, and oxygen absorption  
- High error rates  
- No information on degradation pathways or products | Auta et al. (2018), Balestri et al. (2017), Hintersteiner et al. (2015), Lambert et al. (2013a, 2013b), Ter Halle et al. (2016) |
| Thermoanalytical methods (e.g., TGA, DSC) | Mass-based; 0–20 mg | Changes in thermal properties and stability | - 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 | - Cannot confirm possible degradation pathways  
- Cannot obtain information on environmental degradation products | Cheremisinoff (1996), Deroine et al. (2014), Dümichen et al. (2014), Musiol et al. (2017) |
| Light microscopy               | >500µm             | Imaging of degraded macropolymer surface, visualization and screening of single microplastic particles | - Simple method for visualization and screening  
- Nondestructive | - Extremely high error rate for sample identification, so must couple with definitive chemical identification methods such as spectroscopy | Burns and Boxall (2018), Eriksen et al. (2013), Löder and Gerdts (2015), Musiol et al. (2017) |
| ATR-FTIR                       | >500µm             | Chemical identification and changes in chemical functionality due to degradation | - Well established and widely used  
- Fast analysis time  
- Nondestructive | - Smaller samples may give too weak a signal  
- Spectral interferences from water may arise  
- Micropolymer particles must be visually sorted, which may introduce bias | Cabernard et al. (2018), Lambert and Wagner (2016b) |
| GPC                            | Mass-based; >~20 mg | Molecular weight metrics and changes in molecular weight distribution with degradation | - Relatively fast and simple sample preparation  
- Can provide overall picture of molecular changes with degradation, as well as information on amount of polymer | - High temperature required for some plastic types—potential induced degradation  
- Potential lower accuracy and difficulties distinguishing polymers for certain polymer types | Biver et al. (2018), Giacomucci et al. (2019), Hintersteiner et al. (2015), Müller et al. (2018), Musiol et al. (2017) |
| FPA-based micro-FTIR           | >10 µm             | Simultaneous visualization, mapping, and chemical identification of polymer particles | - Wide area analyzed, giving large numbers of spectra  
- No visual sorting required  
- Automation possible, removing bias in analysis and allowing detection of smaller particles  
- High resolution and nondestructive | - 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 | Cabernard et al. (2018), Ivleva et al. (2017), Primpke et al. (2017) |

(Continued)
| Method                      | Size range | Information obtained                                                                 | Advantages                                                                                                                                  | Limitations                                                                                           | References and examples of use                                                                 |
|-----------------------------|------------|---------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|
| Raman microscopy            | >1 µm      | Simultaneous visualization, mapping, and chemical identification of polymer particles | - High resolution  
- Little interference from water  
- Fast, automatic data acquisition possible  
- Nondestructive  
- Higher resolution in identification compared with FTIR-based techniques | - 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 | Araujo et al. (2018), Cabernard et al. (2018), Frére et al. (2017), Ivleva et al. (2017), Scheurer and Bigalke (2018) |
| Coulter counter             | 0.4–1200 µm| Particle concentration and size distribution                                             | - Sensitive, consistent, high reproducibility  
- Large concentration range  
- Conductivity-based, so orthogonal to optical techniques | - Spherical model may be used to calculate size  
- Particles must be suspended in electrolyte solution | Demuele et al. (2010), Frydkjær et al. (2017), Lambert and Wagner (2016b), Rhyner (2011) |
| 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 | Eshel et al. (2004), Keck and Müller (2008), Kokalj et al. (2018), Lee et al. (2014), Witt and Röthele (1996) |
| 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 aggregation | - Spherical model  
- Particle concentration measurements may be imprecise  
- Method and sample concentration must be optimized 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) |
| Method | Size range | Information obtained | Advantages | Limitations | References and examples of use |
|--------|------------|----------------------|------------|-------------|-------------------------------|
| AFM    | >10 nm     | Visualization of macropolymer surface morphology and polymer particles | - 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 | - Obtaining a representative sample is difficult  
- Imaging artifacts can be problematic | Iñiguez et al. (2018), Merzel et al. (2019), Moons (2002), Nolte, Hartmann, et al. (2017), Yeo et al. (2009) |
| DLS    | 3 nm–6 µm  | Particle size and size distribution | - Fast and straightforward  
- Accurate for monodisperse suspensions  
- Relatively wide concentration range  
- Can give information on aggregation | - Spherical model  
- Less suitable for heterogeneous samples because of low size resolution and high sensitivity toward larger particles  
- Cannot determine particle concentration  
- Less applicable to complex or unknown samples | Besseling et al. (2017), Filipe et al. (2010), Gigault et al. (2016, 2017), Jillavenkatesa et al. (2001), Ter Halle et al. (2017) |
| SEM    | >3 nm      | Visualization of polymer surface morphology and visualization and characterization of polymer particle shapes and sizes | - High resolution  
- Detailed mapping and visualization  
- Elemental analysis possible if coupled to EDS | - Complex sample preparation, which may alter nature of sample  
- Heavy metal staining usually required  
- Difficult to obtain a representative sample—bias when determining size distributions of heterogeneous particle mixtures | Bootz et al. (2004), Brabazon and Raffer (2010), Nazareth et al. (2019), Oriekhova and Stoll (2018) |
| TEM    | >~1 nm     | Visualization and characterization of polymer particles | - Precise information on particle size and shape  
- Elemental analysis possible if coupled to EDS  
- Very high size resolution | - Complex sample preparation, which may alter nature of sample  
- Heavy metal staining sometimes required  
- Obtaining a representative sample may be difficult  
- Thin sample required | Cole and Galloway (2015), Gigault et al. (2014), Michler (2008), Pyrz and Buttrey (2008), Velzeboer et al. (2014) |

(Continued)
### TABLE 3: (Continued)

| Method         | Size range                  | Information obtained                                           | Advantages                                                                 | Limitations                                                                 | References and examples of use                                      |
|----------------|-----------------------------|----------------------------------------------------------------|---------------------------------------------------------------------------|----------------------------------------------------------------------------|---------------------------------------------------------------------|
| py-GCMS        | Mass-based; 3 ng–0.5 mg     | Identification of polymer type and associated additives         | - Solvent not required, reducing background contamination                  | - Difficulty in analysis of plastics in complex environmental matrix       | Dümichen et al. (2015, 2017), Fries et al. (2013), Hermabessiere et al. (2018), Mintenig et al. (2018), Ter Halle et al. (2017) |
| TED-GCMS       | Mass-based; 200 ng–100 mg   | Identification of polymer type and determination of its mass fraction in an environmental sample | - Direct analysis of polymers in environmental matrix                       | - LoD depends on polymer type                                             | Dümichen et al. (2014, 2015, 2017, 2019), Elert et al. (2017)       |
| Range of chromatography-mass spectrometry techniques | LMW chemical compounds     | Characterization and identification of chemical compounds in unknown mixtures | - Can identify compounds in complex mixtures                               | - Determination of compound structure may not be possible                 | Lambert et al. (2013b)                                               |

TGA = thermogravimetric analysis; DSC = differential scanning calorimetry; FTIR = Fourier-transform infrared; MS = mass spectrometry; AT-R-FTIR = attenuated total reflection-Fourier-transform infrared; GPC = gel permeation chromatography; FPA = focal plane array; LD = laser diffraction; MALD = matrix-assisted laser desorption; 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; IR = infrared; SEM = scanning electron microscopy; EDS = energy-dispersive spectroscopy; TEM = transmission electron microscopy; py-GCMS = pyrolysis gas-chromatography mass-spectrometry; LoD = limit of detection; TED-GCMS = thermal extraction desorption gas-chromatography mass-spectrometry; LMW = low molecular weight.
et al., 2017; Mintenig et al., 2018); however, it has been highlighted that many AF4 techniques have been optimized using primary particles and that secondary particles may behave differently (Schwaferts et al., 2019). Chromatographic techniques utilized 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 and high-performance liquid chromatography.

For chemical analysis of nano-sized particles, mass spectrometric techniques are crucial. Pyrolysis gas-chromatography mass-spectrometry (py-GCMS) has been used to identify polymer types of plastic particles (Fries et al., 2013; Hermabessiere et al., 2018; Ter Halle et al., 2017) and may reveal changes resulting from degradation (Ter Halle et al., 2017). Thermal extraction desorption gas-chromatography mass-spectrometry can be used to directly analyze and potentially quantify plastic particles in an environmental sample (Dümichen et al., 2014, 2015, 2017, 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, MW information can be obtained using gel-permeation chromatography, which has been used in analysis of microplastics down to 10 µm (Hintersteiner et al., 2015). Differential scanning calorimetry can give information on thermal properties including Tm and Tg (Deroiné et al., 2014; Musiol et al., 2017).

Although most studies have focused 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). In addition, scattering methods have been used to characterize the hydrodynamic radius of polymers in solution (Armstrong et al., 2004). However, while some analyses of water-soluble polymers in environmental matrices have been carried out (see 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, emphasizing the importance of addressing the research need in question (Elert et al., 2017). It is likely that full characterization 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 characterize both particle size and polymer type of nanoplastics in environmental samples within a suggested framework for micro- and nanoplastic analysis. Use of multiple techniques may aid in analysis of diverse polymer degradation products in standard degradation tests when characterizing full rate and route (see 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 standardized methods for determining a 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 characterization 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 recognized that a previous lack of standardization and adequate quality control of techniques for microplastic analysis has hindered progress in assessing their environmental risk (Burns & Boxall, 2018). Moving forward in polymer analysis, further development and standardization 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. Although 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, Peijnenburg, et al., 2017), further development of robust data sets 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 (see Gottschalk et al., 2009) to multimedia (e.g., Meesters et al., 2014) and spatiotemporally resolved (see Domercq et al., 2018; Quik et al., 2015). Recently, fate models have also been applied to micro- and nanoplastics (see Besseling et al., 2017; Nizzetto et al., 2016), 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 modeling (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 ERA approaches is essential. The unique and complex nature of polymers, including their high and distributed MWs, 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 characterization and modeling; 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 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 categorization, highlighting which parameters may be most important both in polymer identification and grouping and for exposure assessment and fate modeling. However, it is clear that limitations and knowledge gaps remain; key research needs 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. In addition, the relative significance of key fate parameters, particularly in polymer identification and in impacting fate behavior, should be assessed 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 prioritization efforts for polymers and subsequent in-depth exposure assessments.
- Research into characterizing 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. 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 standardize validated and reliable analytical methods for characterization of polymers and their degradation products, to measure properties relevant to exposure assessment as well as characterize degradation processes and products for exposure characterization and modeling. For full characterization, 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 characterization 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 focused to provide sufficient levels of information with minimum application of techniques.
- While 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 nanopolymer particles, such as microplastics; and a combination of modeling approaches from both LMW compounds and nanoparticles may be necessary for characterizing the fate of both a solid parent polymer and its chemical degradation products. This will be further supplemented by development of QSAR approaches and data sets for polymers.
- Further research into the critical fate properties of water-soluble polymers and their breakdown products is warranted to better characterize their risk to the environment. This would help to prioritize 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 characterizing 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.

Supporting Information—The Supporting Information is available on the Wiley Online Library at https://doi.org/10.1002/etc.5272.

Acknowledgment—The present review was funded by the Natural Environment Research Council as part of the Adapting to the Challenges of a Changing Environment Doctoral Training Partnership (grant number NE/S00713X/1).

Disclaimer—The authors declare that there are no conflicts of interests.

Author Contributions Statement—All authors contributed to conceptualization of the review study. Gathering of literature data, writing of first draft, and manuscript revision and refinement: Hattie Brunning. Critical manuscript revision and refinement: J. Brett Sallach, Victor Zanchi, Oliver Price, Alistair Boxall.

Data Availability Statement—Data are available on request from the corresponding author (hcbb500@york.ac.uk and alistair.boxall@york.ac.uk).

REFERENCES

Aislaben, M., & Schick, C. (1994). The melting of polymers—a three-phase approach. Thermochimica Acta, 238, 203–227. https://doi.org/10.1016/S0040-6031(94)85211-1
Amiard, J.-C., & Amiard-Triquet, C. (2015). Conventional risk assessment of environmental contaminants. In C. Amiard-Triquet, J.-C. Amiard, & C. Mouneyrac (Eds.) Aquatic ecotoxicology: Advancing tools for dealing with emerging risks (pp. 25–49). Elsevier. https://doi.org/10.1016/B978-0-12-800949-9.00002-4
\(\text{\textregistered}\)Anit, V. V., \(\text{\textregistered}\)Anit, M. P., Kronimus, A., Oing, K., & Schwarzbauer, J. (2011). Quantitative determination of poly(vinylpyrrolidone) by continuous-flow off-line pyrolysis-GC/MS. Journal of Analytical and Applied Pyrolysis, 90, 93–99. https://doi.org/10.1016/j.jaap.2010.10.011
Apostolovic, B., Deacon, S. P. E., Duncan, R., & Klok, H.-A. (2011). Cell uptake and trafficking behavior of non-covalent, coiled-coil based polymer–drug conjugates. Macromolecular Rapid Communications, 32, 11–18. https://doi.org/10.1002/marc.201000434
Araujo, C. F., Nolasco, M. M., Ribeiro, A. M. P., & Ribeiro-Ciarro, P. J. A. (2018). Identification of microplastics using Raman spectroscopy: Latest developments and future prospects. Water Research, 142, 426–440.
Armstrong, J. K., Wenby, R. B., Meiselman, H. J., & Fisher, T. C. (2004). The hydrodynamic radii of macromolecules and their effect on red blood cell aggregation. Biophysical Journal, 87, 4259–4270.
Armot, J. A., & Gabas, F. A. P. C. (2006). A review of bioconcentration factor (BCF) and bioaccumulation factor (BAF) assessments for organic chemicals in aquatic organisms. Environmental Reviews, 14, 257–297. https://doi.org/10.1139/a06-005
Arp, H. P. H., & Knutsen, H. (2020). Could we spare a moment of the spotlight for persistent, water-soluble polymers? Environmental Science & Technology, 54, 3–5.
Auta, H. S., Emenike, C. U., Jayanthi, B., & Fauziah, S. H. (2018). Growth kinetics and biodeterioration of polypropylene microplastics by Bacillus sp. and Rhodococcus sp. isolated from mangrove sediment. Marine Pollution Bulletin, 127, 15–21.
Balestri, E., Menicagli, V., Vallerini, F., & Lardicci, C. (2017). Biodegradable plastic bags on the seafloor: A future threat for seagrass meadows? Science of the Total Environment, 605, 755–763.
Basheer, C., Obbard, J. P., & Lee, H. K. (2005). Analysis of persistent organic pollutants in marine sediments using a novel microwave assisted solvent extraction followed by LC–MS/MS analysis. Journal of Chromatography A, 1068, 221–228.
Bejgarn, S., MacLeod, M., Bogdal, C., & Breitholtz, M. (2015). Toxicity of leachate from weathering plastics: An exploratory screening study with Nitocra spinipes. Chemosphere, 132, 114–119.
Bergmann, M., Mützel, S., Prümpe, S., Tekman, M. B., Traschel, J. L., & Gerdts, G. (2019). White and wonderful? Microplastics prevail in snow from the Alps to the Arctic. Science Advances, 5, 10.1126/sciadv.aax1157
Berliz-Barbier, A., Vauchez, A., Wiest, L., Baudot, R., Vulliet, E., & Cren-Olivé, C. (2014). Multi-residue analysis of emerging pollutants in sediment using QuEChERS-based extraction followed by LC–MS/MS analysis. Analytical and Bioanalytical Chemistry, 406, 1259–1266.
Berrojalibiz, N., Lacorte, S., Calbet, A., Saiz, E., Barata, C., & Dachs, J. (2009). Accumulation and cycling of polycyclic aromatic hydrocarbons in zooplankton. Environmental Science & Technology, 43, 2295–2301.
Besseling, E., Quik, J. T. K., Sun, M., & Koelmans, A. A. (2017). Fate of nano- and microplastic in freshwater systems: A modeling study. Environmental Pollution, 220, 540–548.
European Centre for Ecotoxicology and Toxicology of Chemicals. (2020). Applicability of analytical tools, test methods and models for polymer risk assessment (Ver 1, Technical Report 133-2).

European Chemicals Agency. (2016). Practical guide—How to use and report (Q)SARs (Ver 3.1).

European Chemicals Agency. (2019). Proposal for a restriction: Intentionally added microplastics (Annex XV Restriction Report).

European Commission. (2006). Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the registration, evaluation, authorisation and restriction of chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/273/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC. OJ L 396.

Federle, T. W., Gasior, S. D., & Nuck, B. A. (1997). Extrapolating mineralization rates from the ready CO2 screening test to activated sludge, river water, and soil. Environmental Toxicology and Chemistry, 16, 127–134. https://doi.org/10.1002/etc.5620160205

Felsot, A. S., Unsworth, J. B., Linders, J. B. H. J., Roberts, G., Rautman, D., Harris, C., & Carazo, E. (2011). Agricultural spray drift; assessment and mitigation—A review. Journal of Environmental Science and Health Part B, Pesticides, food Contaminants, and Agricultural Wastes, 46, 1–23.

Filpe, V., Hawe, A., & Jiskoot, W. (2010). Critical evaluation of nanoparticle tracking analysis (NTA) by nanosight for the measurement of nanoparticles and protein aggregates. Pharmaceutical Research, 27, 796–810.

FOCUS Working Group on Surface Water Scenarios. (2001). FOCUS surface water scenarios in the EU evaluation process under 91/414/EEC (EC Document Reference SANCO/4802/2001-rev.2). European Commission.

Fotopoulou, K. N., & Karapanagioti, H. K. (2012). Surface properties of beached plastic pellets. Marine Environmental Research, 81, 70–77.

Frère, L., Paul-Pont, I., Rinnert, E., Petton, S., Jaffré, J., Bihanic, I., Soudant, P., Lambert, C., & Huvet, A. (2017). Influence of environmental and anthropogenic factors on the composition, concentration and spatial distribution of microplastics: A case study of the Bay of Brest (Brittany, France). Environmental Pollution, 225, 211–222.

Fries, E., Dekiff, J. H., Willmeyer, J., Nuelle, M.-T., Ebert, M., & Remy, D. (2013). Identification of polymer types and additives in marine microplastic particles using pyrolysis-GC/MS and scanning electron microscopy. Environmental Science: Processes & Impacts, 15, 1949–1956.

Fröhlich, E. (2012). The role of surface charge in cellular uptake and cytotoxicity of medical nanoparticles. International Journal of Nanomedicine, 7, 5577–5591.

Frydkjær, C. K., Jersven, N., & Roslev, P. (2017). Ingestion and egestion of nanoparticle tracked by analysis (NTA) by nanosight for the measurement of nanoparticles and protein aggregates. Pharmaceutical Research, 27, 796–810.

Galo, V., C., Inyagh, H. I., Menezes, G. B., & Bae, S. (2007). Clay charge reversal effects on aqueous polymer sorption on lateritic soils. Chemosphere, 66, 635–643.

Giacomucci, L., Raddadi, N., Soccio, M., Lotti, N., & Fava, F. (2019). Polyvinyl chloride biodegradation by Pseudomonas citronellolis and Bacillus flexus. New Biotechnology, 52, 35–41.

Gigault, J., El Hadri, H., Reynaud, S., Deniau, E., & Grassl, B. (2017). Asymmetrical flow field flow fractionation methods to characterize submicron particles: Application to carbon-based aggregates and nanoplastics. Analytical and Bioanalytical Chemistry, 409, 6761–6769.

Gigault, J., Pedrono, B., Maxit, B., & Ter Halle, A. (2016). Marine plastic litter: The unanalyzed nano-fraction. Environmental Science: Nano, 3, 346–350.

Gömö, E. F., & Michel, F. C., Jr. (2013). Biodegradability of conventional and bio-based plastics and natural fiber composites during composting, anaerobic digestion and long-term soil incubation. Polymer Degradation and Stability, 98, 2583–2591. https://doi.org/10.1016/j.polymdegradstab.2013.09.018

Goodrich, M. S., Dulak, L. H., Friedman, M. A., & Lech, J. J. (1991). Acute and long-term toxicity of water-soluble cationic polymers to rainbow-trout (Oncorhynchus mykiss) and the modification of toxicity by humic acid. Environmental Toxicology and Chemistry, 10, 509–515. https://doi.org/10.1002/etc.5620100411

Gorbunov, A. A., & Skvortsov, A. M. (1995). Statistical properties of confined macromolecules. Advances in Colloid and Interface Science, 62, 31–108.

Gottschalk, F., Sonderer, T., Scholz, R. W., & Nowack, B. (2009). Modeled environmental concentrations of engineered nanomaterials (TiO2, ZnO, Ag, CNT, fullerenes) for different regions. Environmental Science & Technology, 43, 9216–9222.

Gouin, T., Becker, R. A., Collot, A.-G., Davis, J. W., Howard, B., Inawaka, K., Lampi, M., Ramon, B. S., Shi, J., & Hopp, P. W. (2019). Toward the development and application of an environmental risk assessment framework for microplastic. Environmental Toxicology and Chemistry, 38, 2087–2110.

Guiney, P. D., Woltering, D. M., & Jop, K. M. (1998). An environmental risk assessment profile of two synthetic polymers. Environmental Toxicology and Chemistry, 17, 2122–2130.

Hartmann, N. B., Hüffer, T., Thompson, R. C., Hasselöv, M., Verschoor, A., Daugaard, A. E., Rist, S., Karlsson, T., Brennholt, N., Cole, M., Herling, M. P., Hess, M. C., Ileva, N. P., Lusher, A. L., & Wagner, M. (2019). Are we overestimating the same things again? Recommendations for a definition and categorization framework for plastic debris. Environmental Science & Technology, 53, 1039–1047.

Hennecke, D., Bauer, A., Herrchen, M., Wischerhoff, E., & Gores, F. (2018). Cationic polyacylamide copolymers (PAMs): Environmental half life determination in sludge-treated soil. Environmental Science Europe, 30, Article 16. https://doi.org/10.1186/s12302-018-0143-3.

Hermabessiere, L., Himber, C., Boricaud, B., Kazour, M., Amara, R., Cassone, A.-L., Laurens, M., Paul-Pont, I., Soudant, P., Dequatre, C., Mercea, P., Milana, M. R., Delaunay, V., & Huvet, A. (2017). Optimization, performance, and application of a pyrolysis-GC/MS method for the identification of microplastics. Analytical and Bioanalytical Chemistry, 410, 6663–6676.

Hernandez, L. M., Yousef, N., & Tufenkji, N. (2017). Are there nanoplastics in your personal care products? Environmental Science & Technology, 51, 280–285.

Hidalgo-Ruz, V., Gutow, L., Thompson, R. C., & Thiel, M. (2012). Microplastics in the marine environment: A review of the methods used for identification and quantification. Environmental Science & Technology, 46, 3060–3075.

Hintersteiner, I., Himmelsbach, M., & Buchberger, W. W. (2015). Characterization and quantitation of polyolefin microplastics in personal-care products using high-temperature gel-permeation chromatography. Analytical and Bioanalytical Chemistry, 407, 1253–1259.

Hokstra, E. J., Brand, F., Dequatre, C., Mercier, P., Milana, M. R., Störmer, A., Trier, K., Vitrac, O., Schäfer, A. & Simoene, C. (2015). Practical guidelines on the application of migration modelling for the estimation of specific migration (JRC Technical Report EUR 27529 EN). European Commission. https://doi.org/10.2788/04517

Horton, A. A., Walton, A., Spurgeon, D. J., Lahive, E., & Svendsen, C. (2017). Microplastics in freshwater and terrestrial environments: Evaluating the current understanding to identify the knowledge gaps and future research priorities. Science of the Total Environment, 586, 127–141.

Hüffer, T., Praetorius, A., Wagner, S., von der Kammer, F., & Hofmann, T. (2017). Microplastic exposure assessment in aquatic environments: Learning from similarities and differences to engineered nanoparticles. Environmental Science & Technology, 51, 2499–2507.

Human & Environmental Risk Assessment on Ingredients of European Household Cleaning Products. (2004). Alcohol ethoxysulfates (AES) environmental risk assessment.

Human & Environmental Risk Assessment on Ingredients of European Household Cleaning Products. (2009). Alcohol ethoxysulfates (Ver 2.0).

Human & Environmental Risk Assessment on Ingredients of European Household Cleaning Products. (2011a). Polyacrylate/sodium acrylate copolymers used in detergents (part I): Polyacrylic acid homopolymers and their sodium salts (CAS 9003-04-7) (Ver 3.0).

Human & Environmental Risk Assessment on Ingredients of European Household Cleaning Products. (2011b). Polyacrylate/maleic acid copolymers and their sodium salts (CAS 52255-49-9) (Ver 3.0).

Huppertsberg, S., Zahn, D., Pauels, F., Reemtsma, T., & Kneppe, T. P. (2020). Making waves: Water-soluble polymers in the aquatic
Moons, E. (2002). Conjugated polymer blends: Linking film morphology to performance of light emitting diodes and photodiodes. Journal of Physics: Condensed Matter, 14, 12235–12260.

Morét-Ferguson, S., Law, K. L., Proskurovski, G., Murphy, E. K., Peacock, E. E., & Reddy, C. M. (2010). The size, mass, and composition of plastic debris in the western north Atlantic Ocean. Marine Pollution Bulletin, 60, 1873–1878.

Moroshishi, T., Ori, T., Aiso, H., Suzuki, T., Okura, T., & Sato, S. (2018). Biofilm formation and degradation of commercially available biodegradable plastic films by bacterial consortia in freshwater environments. Microbes and Environments, 33, 332–335.

Müller, A., Becker, R., Dorgerloeh, U., Simon, F.-G., & Braun, U. (2018). The effect of polymer aging on the uptake of fuel aromatics and ethers by microplastics. Environmental Pollution, 240, 639–646.

Musiol, M., Rydz, J., Janeczek, H., Radecka, I., Jiang, G., & Kowalczuk, M. (2017). Forensic engineering of advanced polymeric materials part IV: Case study of o xo-biodegradable polyethylene commercial bag—Aging in biotic and abiotic environment. Waste Management, 64, 20–27.

Muthukumar, T., Aravinthan, A., Lakshmi, K., Venkatesan, R., Vedaprapaksh, L., & Doble, M. (2011). Fouling and stability of polymers and composites in marine environment. International Biodeterioration & Biodegradation, 65, 276–284.

Nazareth, M., Marques, M. R. C., Leite, M. C. A., & Castro, I. B. (2019). Commercial plastics claiming biodegradable status: Is this also accurate for marine environments? Journal of Hazardous Materials, 366, 714–722.

Nguyen, B., Claveau-Mallet, D., Hernandez, L. M., Xu, E. G., Farner, J. M., & Tufenkji, N. (2019). Separation and analysis of microplastics and nanoparticles in complex environmental samples. Accounts of Chemical Research, 52, 858–866.

Nizzetto, L., Bussi, G., Futter, M. N., Butterfield, D., & Whitehead, P. G. (2016). A theoretical assessment of microplastic transport in river catchments and their retention by soils and river sediments. Environmental Science: Processes & Impacts, 18, 1050–1059.

Nolte, T. M., Hartmann, N. B., Kleijn, J. M., Gamaes, J., van de Meent, D., Hendriks, A. J., & Baun, A. (2017). The toxicity of plastic nanoparticles to green algae as influenced by surface modification, medium hardness and cellular adsorption. Aquatic Toxicology, 183, 11–20.

Nolte, T. M., Peijnenburg, W. J. G. M., Hendriks, A. J., & van de Meent, D. (2017). Quantitative structure–activity relationships for green algae growth inhibition by polymer particles. Chemosphere, 179, 49–56.

Oldenkamp, R., Hoeks, S., Cengiç, M., Barbarossa, V., Bums, E. E., Boxall, A. B. A., & Ragas, A. M. J. (2018). A high-resolution spatial model to predict exposure to pharmaceuticals in European surface waters: ePIE. Environmental Science & Technology, 52, 12494–12503.

Organisation for Economic Co-operation and Development. (1981). Test No. 110: Particle size distribution/ fibre length and diameter distributions. OECD Guidelines for the Testing of Chemicals.

Organisation for Economic Co-operation and Development. (1991). OECD definition of polymer. Second meeting of the OECD expert group on polymer definition: Chairman’s Report (ENV/MC/CHEM(91)18). http://www.oecd.org/env/ehs/oecddfinitionofpolymer.htm

Organisation for Economic Co-operation and Development. (1996a). Test No. 118: Determination of the number-average molecular weight and the molecular weight distribution of polymers using gel permeation chromatography. OECD Guidelines for the Testing of Chemicals.

Organisation for Economic Co-operation and Development. (1996b). Test No. 119: Determination of the low molecular weight content of a polymer using gel permeation chromatography. OECD Guidelines for the Testing of Chemicals.

Organisation for Economic Co-operation and Development. (2000). Test No. 120: Solution/extraction behaviour of polymers in water. OECD Guidelines for the Testing of Chemicals.

Organisation for Economic Co-operation and Development. (2002). Test No. 207: Aerobic anaerobic transformation in aquatic sediment systems. OECD Guidelines for the Testing of Chemicals.

Organisation for Economic Co-operation and Development. (2004a). Test No. 111: Hydrolysis as a function of pH. OECD Guidelines for the Testing of Chemicals.

Organisation for Economic Co-operation and Development. (2004b). Test No. 309: Aerobic mineralisation in surface water—Simulation biodegradation test. OECD Guidelines for the Testing of Chemicals.
