

# Accounting for Molecular Weight Distribution Dynamics in the Environmental Fate Assessment of Water-Soluble Polymers

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**Abstract:** Water-soluble polymers (WSPs) are widely used in industrial and agricultural applications, as well as in consumer products. After use, they may be released into both engineered and natural environments, where their fate is governed by transfer and transformation processes which are strongly influenced by their molecular weight distribution (MWD). Unlike traditional low molecular weight organic chemicals, WSPs are ensembles of molecules with varying chain lengths. This work suggests the use of Monte Carlo (MC) simulations to model shifts in MWDs resulting from abiotic and biotic chain scission reactions in receiving environments. We specify key factors influencing chain-scission selectivity, including chain-end scissions, molecular weight-dependent scissions, and site-specific scissions. Experimental validation of MC simulation predictions presents analytical challenges, requiring high-resolution MWD characterization of WSPs and reliable extraction techniques from complex environmental matrices. MC simulations may play a pivotal role not only in identifying the most relevant molecular weight (MW) ranges for targeted analysis but also in predicting and elucidating environmental chain scission processes.

**Keywords:** Biodegradation · Environmental fate · Molecular weight distribution · Water-soluble polymers



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## 1. Introduction

Water-soluble polymers (WSPs) are widely used in many home and personal care products, industrial applications, and in agricultural formulations, with annual production in Europe alone estimated at several million tons.<sup>[1]</sup> After use, WSPs from consumer products like shampoos and creams<sup>[2]</sup> or from textile finishing<sup>[3]</sup> often enter wastewater treatment plants *via* down-the-drain pathways. If not completely removed during wastewater treatment, a fraction of the WSPs may enter freshwater systems.<sup>[4]</sup> Additionally, WSPs adsorbed to sludge repurposed as fertilizer<sup>[5]</sup> may be transferred to agricultural fields. Input to agricultural soils can also occur directly through agricultural spray formulations in which WSPs serve to ensure efficient delivery of agrochemicals and fertilizers.<sup>[6]</sup> Despite the above WSP release pathways,

the environmental fate of WSPs remains poorly studied and understood.<sup>[7]</sup>

The broad research field of environmental organic chemistry has, over the past decades, developed substantial expertise on linking the chemistry of low-molecular-weight (LMW) organic compounds to their environmental fate. Assessing the environmental fate of WSPs, however, requires considering not only their chemical structure - such as monomer composition and arrangement - but also their molecular weight distribution (MWD). The MWD is commonly described by the number-average molecular weight ( $\bar{M}_n$ ) and the polydispersity index (PDI) (schematics are shown in Fig. 1). These MWD characteristics are dependent on the polymerization mechanism and synthesis method.<sup>[8]</sup> Thus, in contrast to LMW compounds with a single chemical structure, WSPs are an ensemble of molecules with chemically identical building blocks but spanning a range of MWs. Considering MWDs of WSPs in fate assessments calls for extension of the tools and theories used in environmental organic chemistry. For instance, fate models need to explicitly account for the MWD of WSPs (which was not necessary when modelling the fate of LMW chemicals).

When assessing the environmental fate of WSPs, it is essential to consider not only their initial MWD at the time of release but also how this distribution changes over time due to biotic and abiotic chain scission reactions in the receiving environment. These reactions gradually shift the MWD towards smaller MWs, significantly influencing key fate processes such as mobility, surface interactions, and further transformations. The rates and extent of these chain scission reactions - and thus the degree to which the MWD is altered - are strongly influenced by the polymer backbone chemistry. WSPs with hydrolysable or photochemically cleavable backbone bonds are more reactive, while those with chemically inert carbon-carbon bonds tend to be more stable. For those WSPs that have reactive backbone bonds, the result-

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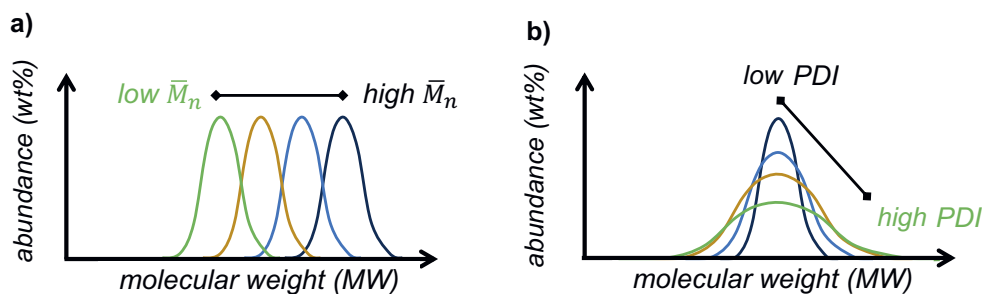


Fig. 1. Fundamental characteristics of the molecular weight distribution of water-soluble polymers include of the a) initial number average molecular weight  $\bar{M}_n$  and b) the polydispersity index (PDI).

ing shifts in their MWD depend strongly on the chain scission reaction mechanism: the shifts may involve a uniform decrease in MW, the formation of a bimodal MWD, or even highly selective formation of specific, well-defined chain fragments. For instance, random chain scission tends to produce a broad range of lower-MW scission products, while if continuous hydrolytic scissions occur at the chain ends (*e.g.* by exolytic enzymes) the MWD may remain unimodal but progressively shifts towards a lower  $\bar{M}_n$ .

Fig. 2 illustrates the importance of chain scission-induced MW decrease in biodegradability assessments. For many high-MW WSPs, extracellular chain scission is the initial, often essential, step to produce products small enough for microbial uptake. These products are then metabolized intracellularly under formation of  $\text{CO}_2$  and new microbial biomass. Biodegradation can be considered the ultimate end point of WSP transformation, ensuring that WSPs are removed in their entirety from the receiving environment. In addition to the above transformation processes (including biodegradation), transfer processes are expected to also strongly depend on MW. For instance, lower MW fractions are expected to exhibit higher diffusivity in porous media, such as soils and sediment, due to their smaller hydrodynamic radii, allowing them to more easily pass into and out of pores.<sup>[9]</sup> At the same time, lower MW products are expected to adsorb less strongly to solid-water interfaces as the interactions (*e.g.* from hydrogen bonding, van der Waals forces, and electrostatics) scale with MW.<sup>[10,11]</sup> As a consequence, adsorption is expected to also be more reversible for low MW polymers compared to high MW analogues.

Given the critical role of MWD dynamics in the environmental fate of WSPs, this contribution aims to outline key considerations for integrating fundamental polymer chemistry into environmental fate assessments of WSPs. We will focus on MWD dynamics, highlighting both computational (*in silico*) and experimental

advancements necessary to predict, measure, and interpret MWD shifts and, thereby, advance our understanding of the fate of WSP. Our suggestions will be supported by experimental and computational results reported in forthcoming publications.

## 2. Probabilistic Modelling of Molecular Weight Distributions

Stochastic approaches, particularly Monte Carlo (MC) simulations, have emerged as powerful tools for modelling MWD dynamics in polymer synthesis.<sup>[12,13]</sup> These methods account for the probabilistic nature of polymer chain formation by simulating individual reaction events. These approaches were also successfully applied to polymer chain scissions in engineered environments, such as abiotic wastewater treatment<sup>[14]</sup> or advanced recycling processes.<sup>[15]</sup> These systems often have (semi-) controlled conditions that make detailed modelling of reactions possible. We aim to highlight the potential of MC simulations in modelling and predicting WSP chain scissions also in natural environments.

Any MC simulation of WSP chain scissions requires defining the starting conditions. The initial MWD of the polymer must be defined by specifying the total number of simulated chains  $N$ , with each chain  $i \in \{1, 2, \dots, N\}$  having an assigned length  $n_i$  representing the number of monomer units in the chain  $n$ , with the MW of the chain being the product of  $n$  and the MW of the monomeric unit,  $MW_{monomer}$ , while accounting for the specific MW of end-groups.

A second parameter to be specified in the MC simulation is the total number of chain scissions  $S$  at which the simulation is terminated. MC simulations thereby allow chain scissions to be followed on the level of individual WSP molecules, while - when taking these molecules back into the entire ensemble - providing insights into the dynamics of the overall MWD as a function of  $S$ . At each iteration of the simulation, a chain  $i$  is

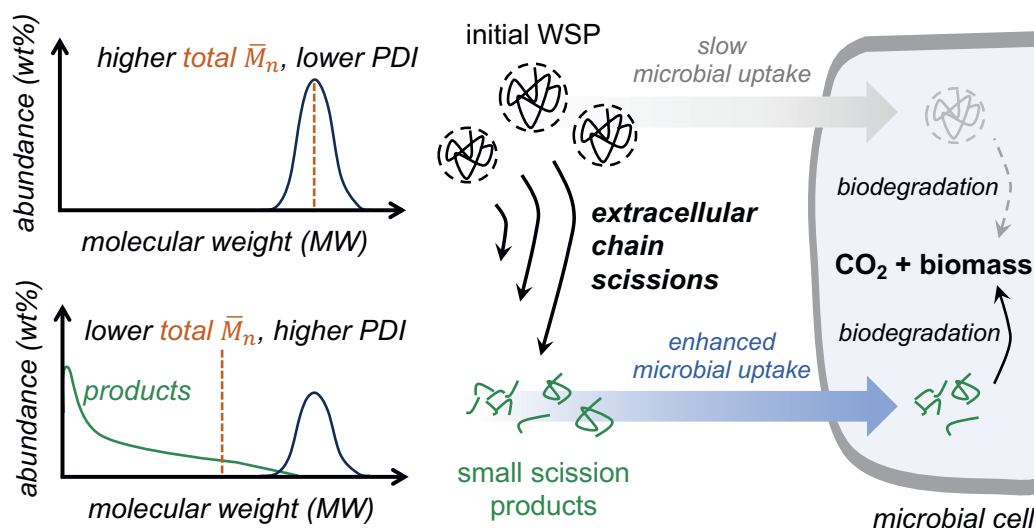


Fig. 2. Sequence of extracellular breakdown through chain scissions, microbial uptake, and intracellular metabolic utilization of water-soluble polymers (WSP). The schematics on the left highlight shifts in the molecular weight distribution (MWD) caused by chain scissions. PDI = polydispersity index;  $\bar{M}_n$  = number average molecular weight.

selected for scission with a certain probability  $P_i$ , with  $\sum_{i=1}^n P_i = 1$ .  $P_i$  can be specified as a function of the chain length  $n_i$  (i.e.  $P_i(n_i)$ ) or can depend on other chain-specific properties (e.g. degree of branching). Following chain selection, the position of the scission in the chain is modelled. The position can be defined as a vector,  $\vec{k}_i = [k_{i,1}, k_{i,2}, \dots, k_{i,n_i-1}]$ , where  $k_{i,j}$  represents a possible scission position along the  $i$ -th chain ( $n_i-1$  cut points for a chain  $i$  with length  $n_i$ ). The probability of selecting a specific scission point  $k_{i,j}$  within  $\vec{k}_i$  is denoted as  $P(k_{i,j})$ , with  $\sum_{j=1}^{n_i-1} P(k_{i,j}) = 1$ .  $P(k_{i,j})$  must be defined as a function of  $\vec{k}_i$  and depends on the scission reaction mechanism. We illustrate four possible scenarios for chain-length specific selection and the corresponding scission point probabilities during scission events in Fig. 3 a-b.

In the first scenario, chains are randomly selected (Fig. 3a, grey): all chains in the ensemble thus have equal probability for selection, regardless of their MW. One example that may be approximated by this scenario is chain-end scission reactions, such as the proposed exolytic enzymatic chain shortening mechanism in polyethylene glycol (PEG) biodegradation.<sup>[16,17]</sup> Since each linear PEG molecule has two chain ends, and if cleavage occurs exclusively at these end groups, then – in a simplified scenario – all chains, regardless of length, would have an equal probability for selection. It is readily apparent how powerful MC simulations can be in this specific example when aiming to predict slow-down of this reaction by end-group passivation, for instance through end-group alkylation of a subpopulation of PEG chains.

The second scenario is that the probability of a chain being selected increases with chain MW (Fig. 3a, orange), as observed in reactions between free radicals and polymer chains. Here, the reaction rate constant scales linearly with the degree of polymerization.<sup>[18]</sup> In this example, the scission position along the chain may also be random (i.e. constant  $P(k_{i,j})$  over  $\vec{k}_i$ ) if the radicals are highly reactive and non-selective (Fig. 3b, black). For instance, hydroxyl radicals, key environmental oxidants generated through photochemical or dark redox reactions, drive non-selective oxidations that lower the MWDs of PEGs in natural systems.<sup>[19]</sup>

In the third case, the probability of a chain to be selected for mechanical scission, for instance caused by shear forces during ultrasonic degradation, increases with increasing MW, reflecting the higher susceptibility of larger than shorter chains to mechanical stress (Fig. 3a, blue).<sup>[20]</sup> Shear forces preferentially occur near the middle of the chains, as the likelihood of entanglement and mechanical stress is greater in these regions due to increased tension and restricted mobility compared to the ends (Fig. 3b, blue).<sup>[21]</sup> While such shear forces may not be a major factor in determining the fate of WSPs in the environment, they may become relevant during analytical sample workup (e.g. when sonicating samples) and may create artifacts in MWD determination if not accounted for.

The fourth case highlights site-specific scission positions along selected chains, resulting in a much larger probability of this site to be selected in the chain (Fig. 3b, green). An example is monomethoxy-poly(ethylene glycol)-block-poly (caprolactone)

(MPEG–PCL) di-block copolymer micelles. Here, enzymatic hydrolysis preferentially targets the PCL core, while non-enzymatic hydrolysis of the PCL occurs preferentially at the PEG-PCL interface.<sup>[22]</sup> Comparing (dynamics in) MWDs in experiments with those generated in MC simulations may thus help determine the relative contributions of individual reaction mechanisms to the total chain scissions. Such a comparison, however, requires experimental data on MWDs with very high MW resolution of individual molecules. Such data remains analytically challenging to obtain and requires methodological advancements.

### 3. Experimental Validation of Probabilistic Models

High-resolution MWD measurements of WSPs are needed for comparison with (and validation of) MC simulations. Commonly, MWD data is obtained from gel permeation chromatography (GPC) which separates dissolved polymers based on their hydrodynamic radii. GPC has been used to analyze polymers with MWs ranging from approximately 100 to 10 million Daltons. However, the GPC resolving power on MW is in many cases expected to be insufficient to yield data suitable for comparison with MC simulations. It is in the field of mass spectrometry (MS) that advances, such as matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) MS, have substantial power to provide highly resolved (down to individual  $n$ ) MWD data. MALDI-TOF MS analyses are relatively rapid and provide absolute MWs, which is essential for characterizing MWDs. Yet, variations in ionization efficiencies between molecules with different MWs or degrees of functionalization can make quantification challenging.<sup>[23]</sup> Recent work has advanced low gradient high-performance liquid chromatography (HPLC) coupled with charged aerosol detection (CAD) as a powerful alternative for polymer analysis.<sup>[24]</sup> CAD is a particularly powerful detector because it provides consistent response factors for non-volatile analytes irrespective of their MW, enabling accurate quantification, also for WSPs containing no chromophores. The uniform response of CADs for WSPs across MW allows accurate quantification of unknowns using a surrogate calibration curve, unlike the compound-specific calibration required in UV or MS detection. When CAD and MS are used in parallel, MS can be employed to identify the polymer, while CAD ensures accurate quantification. For polyethylene glycols (PEG), HPLC-CAD methods were developed offering high resolution while allowing the quantification of individual PEG chains.<sup>[24]</sup>

### 4. Outlook

Combining MC simulations with experimental data to study MWD dynamics of WSPs is anticipated to provide a clearer picture on the importance of WSP MW on environmental fate processes. Further progress in high-resolution MWD analytical methods will improve the ability to validate simulation predictions and better characterize chain scission reaction mechanisms. This progress needs to be matched by developing effective extraction techniques for WSPs from environmental samples, including WSP molecules potentially adsorbed to solid-water interfaces in natural samples. These advancements and the adoption of polymer science prin-

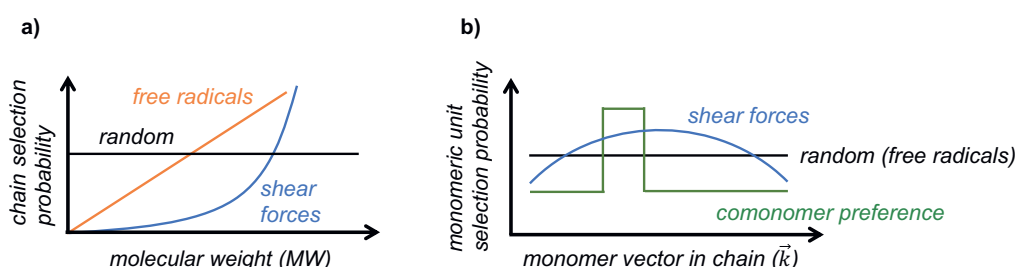


Fig. 3. Illustrating the Influence of a) molecular weight dependent chain selection probabilities and in b) chain position (represented by  $\vec{k}$ ) specific monomer selection probabilities.

principles will prove critical in assessing the fate and biodegradability of WSPs in engineered and natural receiving environments.

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