BUILDING A HOLISTIC KINETIC MONTE CARLO MODELING FRAMEWORK FOR ACHIEVING CARBON CIRCULARITY IN VINYL COPOLYMERS

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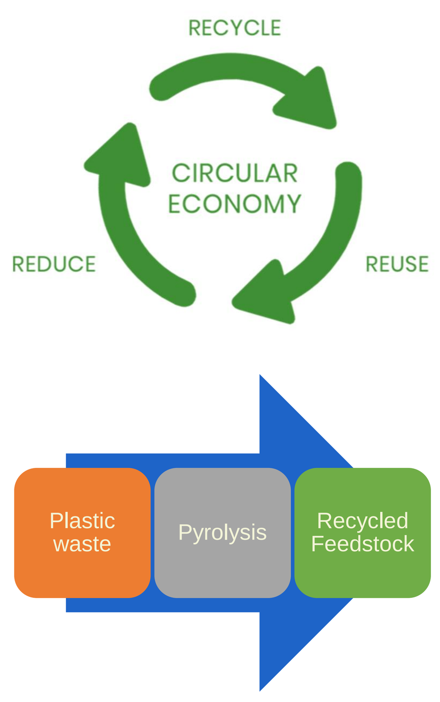
LCT DRIVING CHEMICAL TECHNOLOGY

Introduction and Motivation

- Over the last decades, technological advances, population increase, and lifestyle changes have increased the amount of municipal solid waste (MSW) drastically, in which solid plastic waste (SPW) constitutes a significant part.
- Chemical recycling technologies, e.g. solvolysis, pyrolysis, and reactive extrusion, are likely important contributors to solve the challenge of SPW disposal via monomer/oligomer recovery and polymer upcycling within the circular economy approach.
- Detailed kinetic models for SPW chemical degradation are required to gain fundamental understanding and improve chemical recycling process design and performance.
- A major challenge is to predict the chemical kinetics at the elementary reaction level. In addition, reliable values of numerous kinetic rate coefficients are needed for these reactions and the distributed nature of macrospecies should be accounted for.



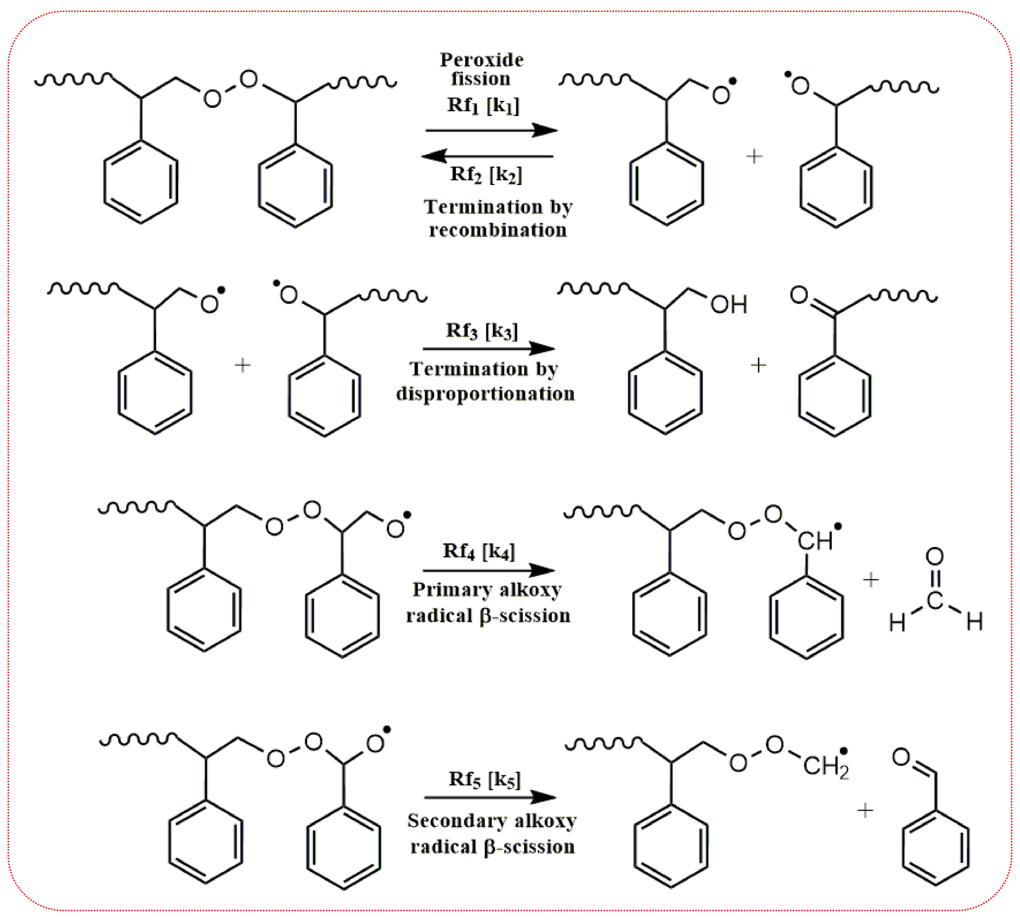
Modeling Approach

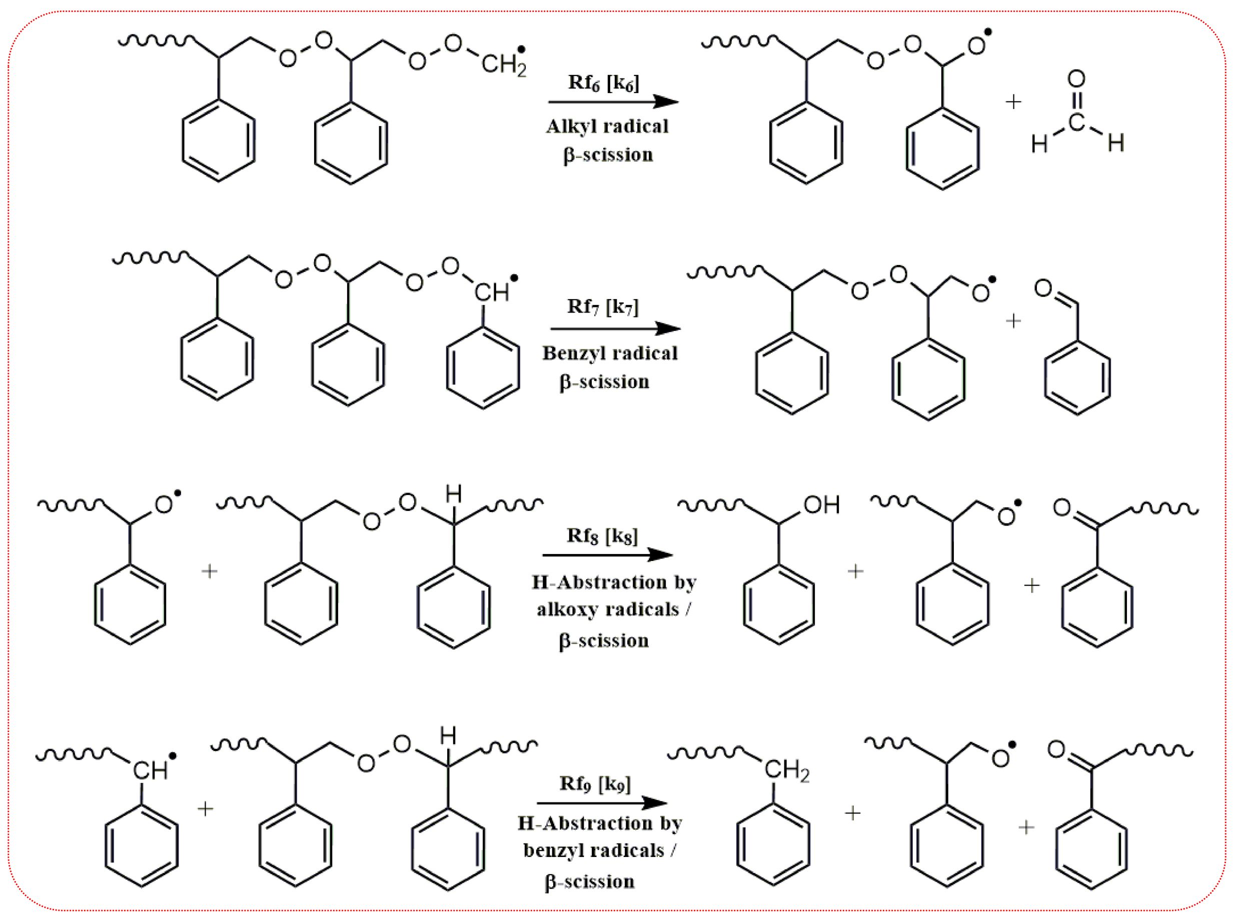
- In this work, we illustrate that with a tree-based approach the temporal evolution of the complete MMD/CLD is within reach.
- In general number-weighted trees [3] are utilized but for fundamental kMC sampling of peroxide bond fissions and hydrogen abstractions, so-called mass-weighted binary trees are implemented.
- An additional novelty to the literature of detailed kinetic models of polymer degradation is the use of ANNs to fine-tune the kinetic parameters, compared to the usual approach of using ANNs to directly predict the final outcomes, i.e. without relying on any mechanistic information, experimental responses, or data.
- The kMC model is validated against the reported evolution of the peroxide bond content and product distributions. Hence, the present work sets out the guidelines to conduct tree-based kMC modeling to understand degradation kinetics with maximal access to distributed information.

Keywords: Polymer degradation, chemical recycling, kinetic Monte Carlo, poly(styrene peroxide)

Model Development

Implemented Reaction Families and End-Groups of Macrospecies





End-group of dead Species or non-reactive end-group radical species			Reactive end-group of radical Species		
Name	Indicator next to x	Structure	Name	Indicator next to x	Structure
Primary Carbon	P_{x1}		Primary Alkoxy Radical	R_{x1}	
Benzylic Carbon	P_{x2}		Secondary Alkoxy Radical	R_{x2}	
Primary Hydroxide	P_{x3}		Primary Alkyl Radical	R_{x3}	
Primary Carbonyl	P_{x4}		Secondary Benzyl Radical	R_{x4}	
Secondary Hydroxide	P_{x5}				
Secondary Carbonyl	P_{x6}				

Each species has two end-groups with at least one repeating PSP unit.

Simulation Results

Parameter Tuning Through ANNs and Model Validation

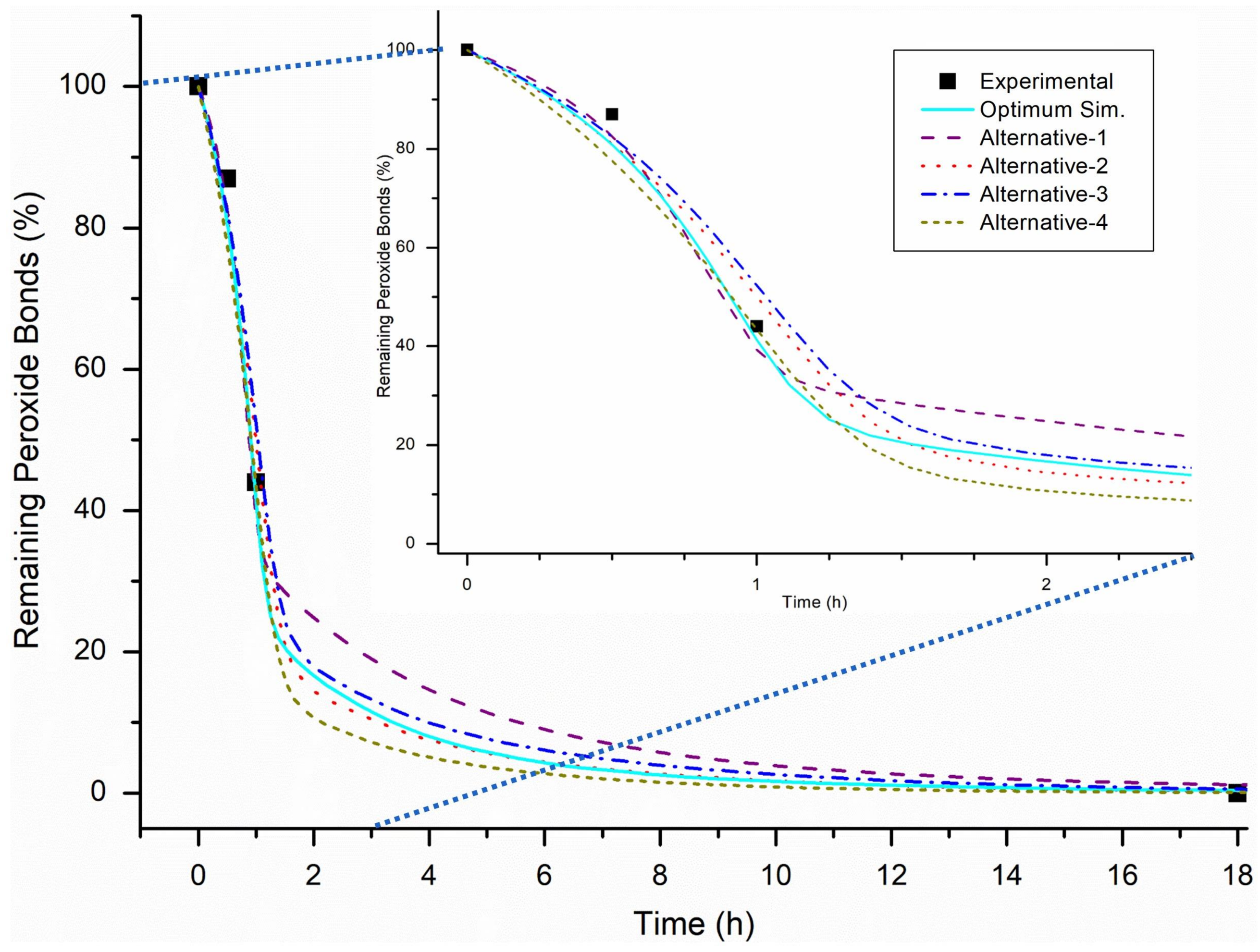


Figure 1: Peroxide bond evolution of the favorable simulations obtained using the parameter tuning methodology. Literature data are used. [1]

- By making use of the parameter tuning methodology with ANNs, multiple rate coefficient sets can be discovered to successfully mimic the literature experimental data of remaining peroxide bonds within experimental error limits.
- Upon tuning to the experimental peroxide bond profile, shown in **Figure 1**, out of a total of 865 simulations the optimum favorable rate coefficient set corresponding to the cyan solid line in the Figure was chosen.
- Alternative sets are possible as illustrated by the 4 extra lines in **Figure 1**.
- The simulated yields (upon grouping) benchmark favorably against the experimental data from Mayo and Miller, [1] as highlighted in **Figure 2**.

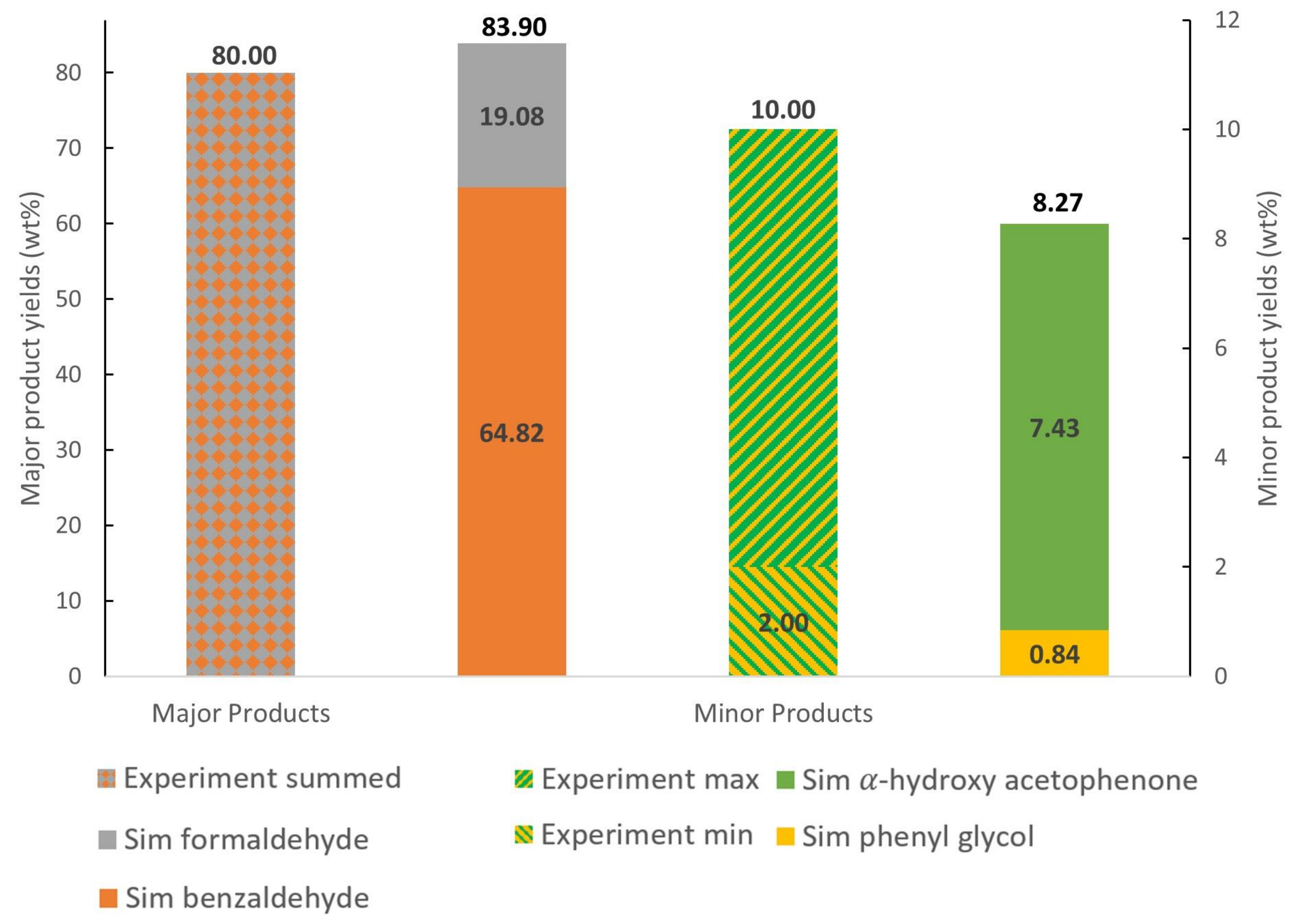
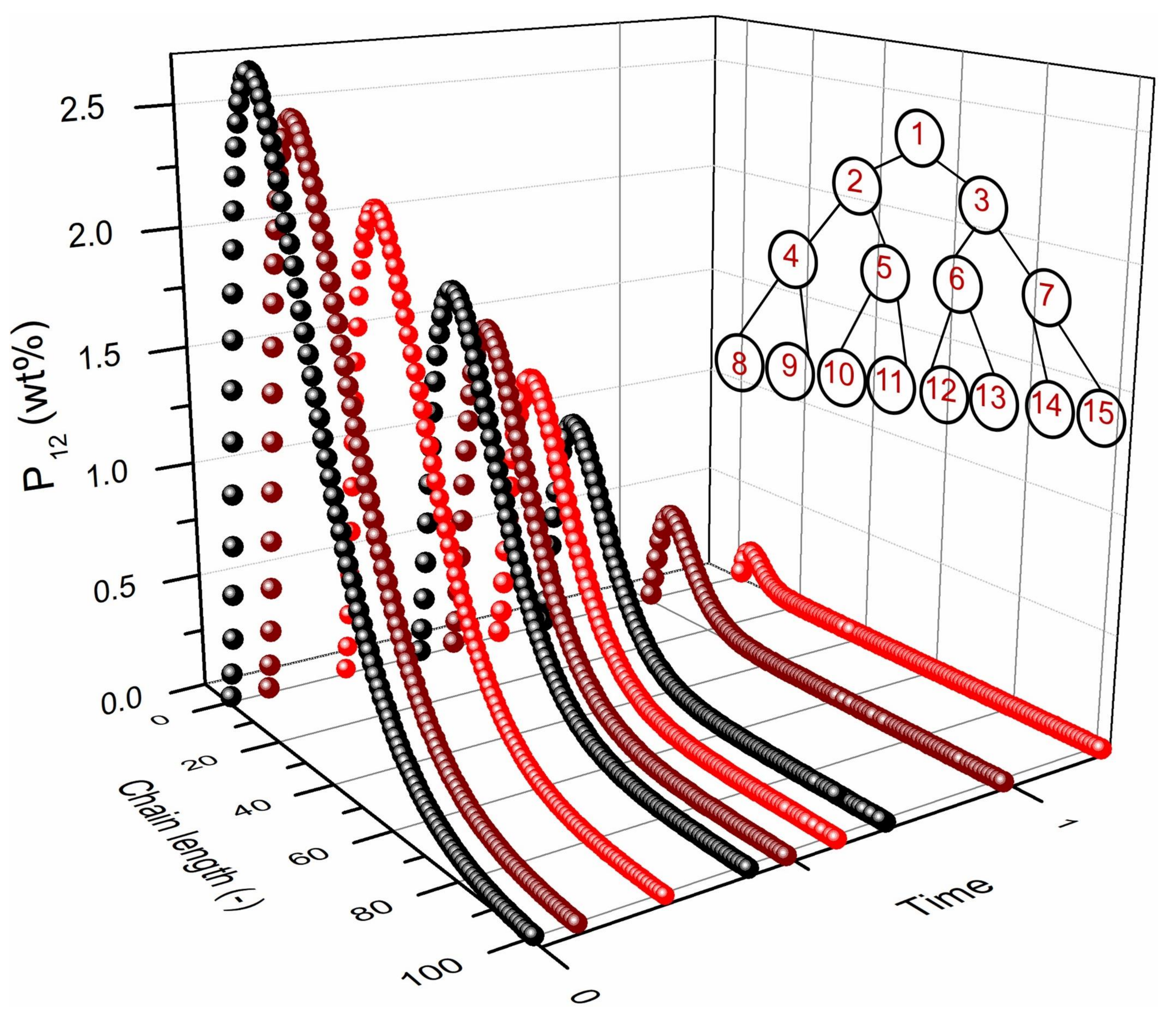


Figure 2: The comparison of simulation and experimental yields [1] for major and minor products.

Time-resolved CLDs



Conclusions

- A tree-based kMC model considering 9 reaction families for the isothermal degradation of polydisperse PSP was developed to demonstrate its potential to track distributed properties and product yields as a function of reaction time.
- Such implementation allowed to fine-tune the rate coefficients and achieve physically realistic values with the help of ANN models.
- The choice for PSP is motivated by the well-defined radical initiation step at the peroxide bonds, which allows us to focus on the kinetics of the unzipping steps.
- The model benchmarks favorably against the experimentally reported evolution of the peroxide bond content and product distributions.
- The ANN driven sensitivity analysis and fine-tuning strategy is also utilized to help to unravel the effects of individual reactions on the experimental responses and other simulation outputs.
- The kMC approach combined with the AI tool is impeccably capable of unraveling the kinetics behind the PSP degradation process.
- This proof-of-concept modeling approach can thus be safely applied to model the degradation of polymers abundant in solid plastic waste (SPW) such as polyethylene (PE) and polystyrene (PS) of which the initiation step is less defined because it involves structural defects in the backbone.

References

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