

DEVELOPING STRATEGIES FOR POLYMER REDESIGN AND RECYCLING USING REACTION PATHWAY ANALYSIS

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Abstract

The current lack of sustainability of and the limited portfolio of recycling processes for synthetic polymers have posed serious threats to the environment. Approximately 90% of plastics are produced via fossil fuels, and over 150 million tonnes of plastics have been discarded in the ocean. Annual production of plastics is expected to reach over 1 billion tons in 2050, but the current manufacturing, consumption, and disposal schemes of fossil-based polymers follow an unsustainable framework. Using reaction pathway analysis, we are pursuing a portfolio of strategies for redesign and recycling of polymers for sustainability. We focus on design of polymers that have accessible operating windows for recovery of monomer, and kinetic modeling frameworks that can be used for process analysis and optimization for polymer recycling.

Keywords

Reaction pathway analysis, kinetic modeling, kinetic Monte Carlo, population balance modeling, polymer recycling.

Introduction

Pyrolysis is a promising method for resource recovery from mixed plastic waste that is compatible with current petrochemical infrastructure that thermally converts polymers in the absence of oxygen into valuable chemical feedstocks and monomer. To provide further insight into polymer pyrolysis, a greater understanding of the mechanistic and kinetic details of the underlying reaction network is needed. To handle the complexity of mechanistic modeling of polymer degradation, we have developed both continuum and kinetic Monte Carlo (kMC) models. We have applied these approaches to study the degradation of polystyrene, polypropylene, polyisoprene, polystyrene peroxide and binary mixtures, and we are able to capture diverse experimental measures, including yields of individual low molecular weight products, as a function of reaction conditions. In order to solve the large models that are created, values of the rate coefficients for $O(10^5)$ reactions are typically required. The approach that we have developed to specify rate coefficients is hierarchical, based on a combination of literature values, estimation methods, and computational chemistry.

Alternatively, redesign efforts focusing on polymers that can be reused and recycled to monomers can lead to sustainable solutions for the plastics waste problem. In this

approach, polymers are designed to undergo depolymerization under particular reaction conditions, yielding monomer units that can then be repolymerized for new applications. Density functional theory (DFT) calculations to calculate the thermodynamic properties of a range of circular polymers and their associated monomers are used. Accurate thermodynamic parameters are essential for knowing the ideal conditions for polymerization and depolymerization of circular polymers. Once conditions that favor the formation of monomers thermodynamically are identified, conditions can be designed based on kinetics, using DFT and kinetic modeling to simulate rates and selectivities for monomer(s) formation and reaction conditions under which side reactions are minimized.

Methods

Kinetic modeling

Two distinct approaches for the kinetic modeling of polymer recycling are used: continuum modeling based on population balances and the method of moments, and stochastic simulations using kinetic Monte Carlo. For the complex chemistry of polymer pyrolysis, mechanistic models using continuum approaches are used. Differential

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equations tracking structurally distinct polymer species are developed, and these equations incorporate a wide range of free radical reactions, including reactions leading to specific low molecular weight (< 400 g/mol) products (i.e., the usable products). Elementary steps are included based on the reaction families that characterize pyrolysis chemistry, including bond fission, chain-end β -scission, mid-chain β -scission, 1,5-hydrogen transfer, 1,3-hydrogen transfer, radical addition, radical recombination, disproportionation, and hydrogen abstraction. Unique polymer groups are devised that allowed polymeric features to be tracked while maintaining a manageable model size. Polymer species are lumped into various classes to track the presence and location of radical centers, the position of double bonds, the inclusion of branches, and the orientation of the “head” and “tail” ends of the monomer units. To facilitate model construction, programs based on scripting languages have been developed to assemble model equations from input of the polymeric features to be tracked.

The methodology relies on the method of moments, which are characteristics of the chain length distribution. The method of moments is applied to rate equations based on elementary step kinetics written explicitly in terms of chain length to develop differential equations describing the evolution of the moments. The moment equations are then solved to monitor the molecular weight distribution as a function of time, temperature or other controlling process variable. We distinguish among different types of dead and live species according to the number of branches, the number of double bonds, the “head” or “tail” orientation of the end units, and the position of the radical center to maintain a more direct link between structure and reactivity.

To track even greater detail, kinetic Monte Carlo (kMC) models are formulated. kMC offers advantages over continuum kinetic models that have been used to model de/polymerization reactions, as they are unable to provide detailed, explicit information about the distribution and composition of the macromolecular chains. kMC allows the explicit topology of populations of polymeric chains to be specified, which can be used to provide input to other simulation methods such as molecular dynamics and Monte Carlo for predicting macroscale properties of polymers. Overall, the approach involves formulating the elementary steps underlying de/polymerization and their associated rate coefficients to create a reaction mechanism. This reaction mechanism is coupled with reactor design equations, and the mechanistic model is solved to predict conversion, product yields and molecular weight distribution. Using the Gillespie approach (1976, 1977), the reaction rate for reaction r is calculated by multiplying reactant amount(s) by the rate constant,

$$R_r = c_{ij} N_i N_j \quad (1)$$

Once all N reaction rates are calculated, the rates are summed to determine a propensity function, or the likeliness of a reaction to occur, and a random number selects the reaction.

$$p_r = \frac{R_r}{\sum_{r=1}^N R_r} \quad (2)$$

The summed rates also inform the time step with the relation:

$$\tau = \ln\left(\frac{1}{x}\right) \frac{1}{\sum_{r=1}^N R_r} \quad (3)$$

where τ is the timestep, and x is a uniform random number between 0 and 1. Time advances to $t = t + \tau$. Once a reaction occurs, a stoichiometric number of molecules is added or removed from the respective species counts. The kMC algorithm iterates through a predetermined number of timesteps or until a final time is reached.

Density functional theory for kinetic and thermodynamic properties

Thermodynamic properties and rate coefficients used in the kinetic models are estimated using a hierarchical approach that relies on density functional theory to create correlations and group additivity values and fill gaps in experimental data. All calculations are performed in Gaussian 16 (Frisch et al., 2016) using the MN15 meta-hybrid functional of Truhlar and coworkers. The Def2-SVP basis set is used for first-pass calculations, and the output from this calculation is used as input for higher-level production calculations using the larger Def2-TZVP basis set. While performing geometry optimizations and frequency calculations using a smaller, lower cost basis set as a first pass increases the total number of calculations required, the total computational expense is reduced due to increased efficiency using this approach, as opposed to optimization from scratch at a higher level of theory. Where applicable, solvent effects are modeled using the SCRF solvation model included within Gaussian 16. Thermodynamic properties are calculated using standard formulae from statistical mechanics, and transition state theory is used to calculate rate coefficients.

Results and Discussion

Pyrolysis of polyolefins

Using the method of moments, detailed mechanistic models for a variety of polyolefins have been constructed in the Broadbelt group. Depending on the experimental data that is available to compare the model against, it is feasible to capture the yields of a wide range of small molecules with different molecular weights and functionalities (e.g., saturated and unsaturated). The model can also be used to generate overall rates of decomposition, which can be compared to global experimental data, which encapsulates kinetic parameters of elementary steps into an overall observed rate coefficient in Arrhenius form. Polystyrene is used here as an example system. While the final model tracked 75 species and included over 3500 reactions, and thus 3500 different rate coefficients, the overall behavior could be described by simulating an overall initial rate of decomposition as a function of temperature and regressing a single overall activation energy, which is what is typically reported experimentally from thermal gravimetric methods.

Based on regression of Arrhenius parameters, polystyrene exhibits an overall activation energy of 53.3 kcal mol⁻¹. Note that this value is not the activation energy for bond fission of the polymer backbone, which is often mistakenly cited as the controlling feature of polymer pyrolysis, nor it is the value of any one other individual elementary step in the model. Instead, it is a combination of the parameters of individual elementary steps that reflects the free-radical reactions that collaborate to create kinetic cycles that lead to high rates of decomposition. This overall value can be used in process design and optimization, while the detailed mechanistic model can be reserved for more intense scrutiny of the product quality.

Kinetic Monte Carlo modeling of poly(ethylene terephthalate) glycolysis

A kMC framework to unravel depolymerization pathways of step-growth polymers using poly(ethylene terephthalate) (PET) as an example has been developed. The model comprises three steps: polymer reconstruction, defining reaction networks, and obtaining polymer and product distributions. The Schulz-Flory distribution was used to define the initial population of chains and the maximum chain length, given values of number average and weight average molecular weight for the polymer being decomposed. Further, a set of reaction families that characterize the types of bond cleavage events via glycolysis is defined to allow the formation of intermediate and low molecular weight product (LMWP) species, as shown in Figure 1. Finally, the kMC framework simulates these reactions as single events occurring at discrete time steps, with parameters estimated from density functional theory as initial values and finalized by regression against experimental data.

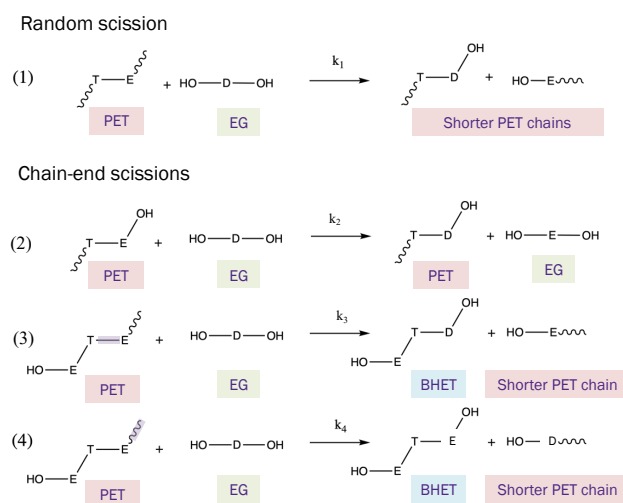


Figure 1. Distinct reaction channels tracked in kMC simulations of PET glycolysis

Uncatalyzed glycolysis data was used to provide a baseline for fitting rate coefficients of all the reaction

events. The neat chemistry was then combined with catalyzed pathways to evaluate the catalyst's effect on the molecular weight decay and the temporal yield of LMWP. Validating the model yields and mapping reaction events suggested that random scissions dominate uncatalyzed glycolysis. On the other hand, competition exists between end-chain scission and random scission in catalyzed glycolysis of PET.

Kinetic Monte Carlo modeling of decomposition of hyperbranched polymers

Hyperbranched polymers based on lactones present intriguing possibilities for recovery of high yields of monomer at accessible reaction conditions. One such possible polymer is represented in Figure 2, which depicts a mechanism for the catalytic depolymerization of one possible end group environment to form the cyclic lactone monomer. 1A is a starting point where the catalyst, TBD, is interacting with both OH groups at the end of the polymer chain. 2A is the pre-reaction complex for the ring closing reaction, which requires a low barrier for formation. TS1A is the ring closing transition state structure, leading to 3A which can be considered as either the product of the ring closing, or the pre-complex for the depolymerization step. Finally, TS2A is the transition state for the depolymerization step and the generation of the monomer product, the M5 lactone, via an intermediate complex 4A. Free energy profiles were calculated at 298.15 K and with a concentration of 1 mol L⁻¹ at the M062X/Def2-TZVP level of theory, including dispersion with the D3 correction. Solvation was included implicitly, and DMSO was chosen as the solvent. The results to date indicate that M5 is both thermodynamically and kinetically favored compared to the alternative lactone at conditions that do not lead to any other side reactions.

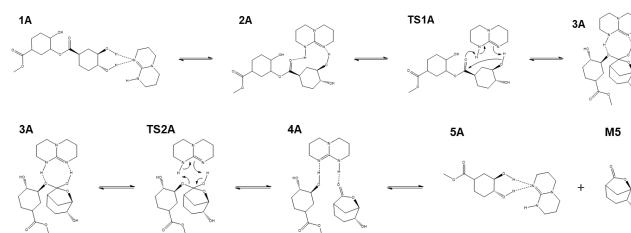


Figure 2. Mechanism for TBD-catalyzed decomposition of lactone-based polymers to form monomer (M5)

Finally, a kinetic Monte Carlo model of inimer polymerization was completed to unravel contributions of chain growth, step growth, and looping reactions, leading to structural models that could be subjected to depolymerization modeling. To ensure that the parameters

governing the polymerization kinetics captured the experimental features (i.e., monomer conversion, degree of branching, and Mn and Mw), a derivative-free optimization method adapted from Gao and coworkers (Gao, 2018) was used. In parallel with these efforts, DFT calculations are in progress to calculate rate coefficients for lactone polymerization for ten representative local environments using the same approach detailed above for the one environment leading to M5 shown in Figure 2.

Conclusions

It is imperative that approaches are developed to address the discarding of plastics. Here, we outline two promising approaches and the role that kinetic modeling and reaction pathway analysis can play in process design and optimization. The first approach is pyrolysis, a technology for thermochemical depolymerization and reclamation of plastic waste. One potential drawback of pyrolysis is that the high reaction temperatures required for degradation of the polymer sample can lead to highly complex reaction networks. In order to obtain maximum atom efficiency and control over product distributions, these reaction networks need to be understood, and the relationships between the formation of low molecular weight compounds fully known. By understanding the routes of formation of these species, insights into appropriate reaction conditions that can promote or impede their formation may be gained, affording greater control over pyrolysis product distributions. In addition, the kinetic model can be a vehicle for predicting global measures of reactivity that then provide quantitative parameters that are compatible with rapid process design and optimization.

The second approach to more sustainable polymer use is through creation of circular polymers. These types of polymers are designed to undergo depolymerization under particular reaction conditions, yielding monomer units that can then be repolymerized for new applications. Density functional theory calculations are an important component to investigating attractive candidates by calculating the thermodynamic properties and kinetic constants of a range of circular polymers and their associated monomers. These values can then be used in kinetic modeling frameworks, including kinetic Monte Carlo, a stochastic simulation approach that allows exquisite detail about polymer topology and the local environment in which labile bonds reside that is well suited to the hyperbranched inimers investigated here.

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