

# MECHANISTIC MODEL OF POLYMER PYROLYSIS

The researchers are developing the theoretical framework necessary for the mechanistic modeling of the decomposition of polymers during pyrolysis.

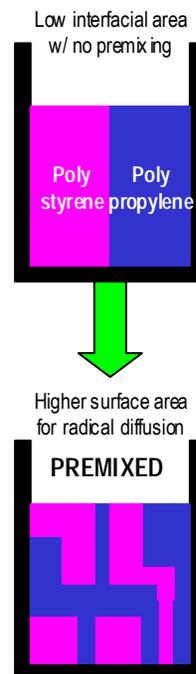
Principal Investigator: Linda J. Broadbelt

**Objective:** The push to recycle plastics, which already comprise 10% (> 30 vol %) of municipal solid waste, has increased dramatically in recent years as environmental concerns over landfill capacity continued to grow. Converting waste polymers to valuable chemicals would be desirable, but the lack of a comprehensive understanding of pyrolysis – a set of reactions, which involve high temperatures, mixed feedstocks, messy radical transformations, and a very complex product distribution – presents a significant obstacle. Mechanistic modeling of the decomposition of individual polymers and polymer mixtures during pyrolysis should allow for objective design of polymer recycling procedures.

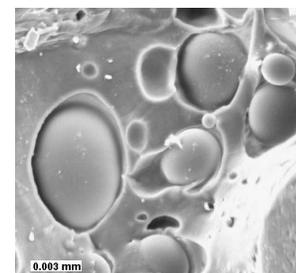
**Approach:** Differential equations describing the kinetics of pyrolysis are generated using the method of moments, and the mechanistic chemistry of pyrolysis is implemented by deriving the terms of the moment equations for the following reactions: (1) chain fission, (2) radical recombination, (3) allyl chain fission, (4) hydrogen abstraction, (5) mid-chain  $\beta$ -scission, (6) radical addition, (7) end-chain  $\beta$ -scission, (8) intramolecular hydrogen transfer, and (9) disproportionation. The frequency factors and the  $E_0$  parameter in the Evans-Polanyi relationship ( $E = E_0 + \Delta H_r$ ) for each reaction type are obtained from the literature. Due to a large number of species and reactions under investigation, a program written in the Perl programming language, is used to construct a list of chemical reactions in the traditional form. A novel parsing program is used to transform this list into moment rate terms, which are then assembled into a set of ordinary differential equations that include three (0<sup>th</sup>, 1<sup>st</sup> and 2<sup>nd</sup>) moment equations for each unique species.

**Results:** The Broadbelt group has successfully simulated pyrolysis of polystyrene (temperature 310-420 °C) using a model that tracked 64 polymeric and low molecular weight (LMW) products and incorporated 2700 individual reactions. Similarly, the researchers have been able to model the yields of the ten main LMW products from the pyrolysis of polypropylene (temperature 350-420 °C) using a model that tracked 130 polymeric and LMW species and incorporated 9100 individual reactions. The individual components of the models for polystyrene and polypropylene are combined to create a binary degradation model for polystyrene and polypropylene mixtures, which captures the 270% enhancement in the polypropylene degradation observed experimentally in polystyrene/polypropylene mixtures. The researchers have also demonstrated that using Solid State Shear Pulverization (SSSP) to blend polystyrene and polypropylene results in a 20% increase in the polypropylene degradation rate compared to no premixing.

**Selected Publications:** Kruse TM, Woo OS, Broadbelt LJ, *Chem. Eng. Sci.* **2001**, 56:971; Kruse TM, Woo OS, Wong, H-W, Khan SS, Broadbelt LJ, *Macromolecules* **2002**, 35:7830; Kruse TM, Wong H-W, Broadbelt LJ *Ind. Eng. Res.* **2003**, *in press*.



Premixing binary mixtures of polystyrene and polypropylene leads to increased degradation rates for polypropylene.



SEM image of SSSP samples showing the intricate mixing of polystyrene and polypropylene.