## 598b Kinetic Modeling of the Effect of Structural Heterogeneities on Polymer Degradation

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Understanding the degradation of polymers has important implications for developing resource recovery strategies, where polymers are degraded intentionally to form high-valued products, and for predicting and controlling the lifetime of polymers during their use. Despite decades of research, there is still debate about the degradation of polyolefins, including polystyrene which has been intensely studied. Ambiguity still remains largely because of the disparate experimental results that are obtained. Most notably, activation energies ranging from 20 to 75 kcal/mol have been reported for the degradation of polystyrene. This wide range of experimental values is often ascribed to heterogeneities in the polymer being degraded. Weak links have often been invoked as the key structural heterogeneity to explain discrepancies in the literature for polymer degradation. However, there are no comprehensive quantitative studies that have examined whether the presence of weak links can account for the observed changes in the degradation behavior.

To understand the effect of weak link heterogeneities quantitatively, we have developed a mechanistic model for the pyrolysis of polystyrene with peroxide bonds as model weak links. The model uses the method of moments to track polymeric species, which are divided based on key structural elements. These include primary carbon, secondary carbon and oxygen end groups, unsaturated moieties (carbon-carbon double bonds and carbonyl groups), and radical position (mid-chain, end-chain, or non-radical species). Low molecular weight species and radicals are tracked explicitly. Elementary reaction types were used to create the terms in the balance equations for each species. Reaction types include (1) chain fission (2) radical recombination (3) hydrogen abstraction (4) mid-chain beta-scission (5) radical addition (6) end-chain beta-scission (7) hydrogen shift and (8) disproportionation. Structure-reactivity relationships were used to link kinetic parameters to the structure and thermodynamics of the reactants and products. The model contains 162 species and tens of thousands of reactions. A broad range of initial peroxide bond concentrations were explored, allowing systems ranging from pure polystyrene to pure poly(styrene peroxide) to be examined, and the results were compared to limited experimental data. The model provided new insights into the effect of weak links on polymer degradation and helped to explain disparate experimental results in the literature.