

## Measurements and Molecular Modeling of Flammability

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**Research Objective:** To guide synthesis of new fire-safe polymers using general principles of flammability chemistry, new milligram-scale test methods, and molecular modeling of polymer decomposition.

**Approach:** First, to guide the search for new fire-safe materials, we classify the chemical features of low-flammability polymers into three areas: resistance to decomposition, low evolution of flammable gases, and formation of char. Then using standard polymers and new polymers generated by UMass synthetic chemists and others, we measure flammability with two apparatus. The first is a flow microcalorimeter developed by Lyon and Walters of the FAA Technical Center, which pyrolyzes a small sample, oxidizes the generated gases, and measures heat release rate from the amount of O<sub>2</sub> depletion. The second, developed here, pyrolyzes a small sample in a commercial TGA/DSC apparatus, sampling the head space just above the sample, analyzing those gases by GC/MS, and measuring heat release rate from the mass loss rate and the gases' heats of combustion. Finally, mechanisms of degradation are inferred from the measurements of kinetics and product gases, quantum-chemistry modeling of the transition states, and reaction modeling.

**Accomplishment Description:** Using data and modeling, we have identified degradation mechanisms for two new polymers that are quantitatively plausible. First, kinetics for polyhydroxyamide (PHA) pyrolysis were measured and predicted (Fig. 1). TGA data were the main source of measured kinetics, analyzed to extract first-order rate constants from temperature-ramped data. Structures and transition states were predicted at a BAC//MP4-6-31G(d,p)//UHF/6-31G(d) level of theory beginning with a model compound, HO-CH=CH-NH-CHO. Formation of polybenzoxazole was indicated to proceed via a keto-imidol shift, a concerted elimination of water, and a concerted ring closure. The measured activation energy was consistent with TGA predictions using integration of the time-dependent equations and the theoretical rate constant. Similarly, a polycarbodiimide was shown to decompose not by homolytic bond fission but rather by concerted pericyclic reaction. Again, agreement with the observed activation energy was quantitative.

**Significance:** The use of degradation mechanisms, quantitative and qualitative, points to useful fire-resistant chemistry and operating ranges for their utility. Likewise the development of new measurement techniques, independently and in collaboration with the FAA, provides flammability testing for small amounts of trial, newly synthesized polymers.

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**Expected Results:** Degradation mechanisms for fire conditions will be developed for new polymers. These quantitative insights will be useful for modeling fires and suggesting new fire-safe polymers.

**References:** Karin Rotem, "Computational Quantum Chemistry Applied to NO<sub>x</sub> Chemistry and New Fire-Resistant Polymers," Ph.D. Dissertation, University of Massachusetts Amherst, Chemical Engineering (1998).

Taline Inguilizian, "Correlating Polymer Flammability Using Measured Pyrolysis Kinetics," M.S. Thesis, University of Massachusetts Amherst, Chemical Engineering (1999).

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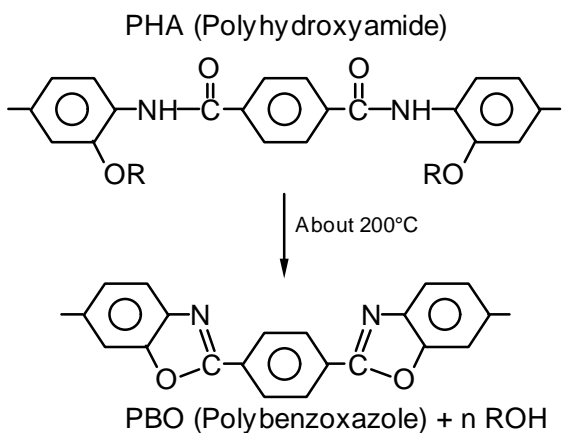


Fig. 1. Overall PHA to PBO reaction.

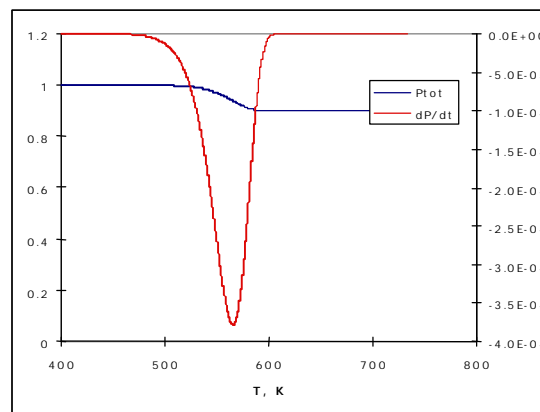


Fig. 2. Simulated TGA curve.