Low Flammability Precursors to Polybenzoxazoles

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Research Objective: To develop novel precursor polymers that can cyclize to polybenzoxazoles and evolve flame-quenchers under fire condition.

Approach: All-aromatic polybenzoxazoles (PBO) have generated considerable interest because of their excellent thermal and thermo-oxidative stability. However, due to their low solubility, these polymers are difficult to process for commercial applications. Precursor polymers, polyhydroxyamides (PHA) and their derivatives have several advantages including more facile processability and being able to adsorb large amounts of energy during cyclization to PBO (Scheme 1). In addition, cyclization is accompanied by the release of small molecules that can act as efficient flame-quenchers.

Accomplishment Description: Polyhydroxyamides (PHA) having high molecular weight (η_{inh}>2.50 in H_2SO_4) and good mechanical properties (tensile strength up to 130 MPa and initial modulus of 5.9 GPa) have been routinely prepared from 3,3'-dihydroxybenzidine and isophthaloyl chloride. TGA data shows only 10 % weight loss at 550 °C and 25 % loss at 900 °C in air. Acyl derivatives (**a**) and phosphorous derivatives (**b** and **c**) were prepared by reacting PHA with corresponding acyl chlorides and chloro phosphates, respectively. Although phosphorous modified PHA's can easily cyclize to PBO, microcalorimeter combustion analyses showed that they released a total heat of 5.1-10.2 KJ/g which is higher than that of unsubstituted PHA (2.1-3.0 KJ/g). More promising results have been shown with the alkyl derivatives (**d**). Above 300 °C the alkoxyamides cyclized to form the corresponding benzoxazoles with loss of the corresponding alcohol. TGA data showed 55 % char yield at 900 °C in nitrogen. Other polymers containing halogen substitution on the alkyl group will be under investigation.

Significance: The ability to synthesize polyhydroxyamides and their derivatives for precursors to polybenzoxazoles provides a low-flammability, high char material for aircraft interior usage as coatings, films, fibers, and wire insulation.

Expected Results: We anticipate that we will prepare halogenated modified PHA precursors that will be processable and also possess exceptional low flammability properties at least equivalent to the best polybenzoxazoles.

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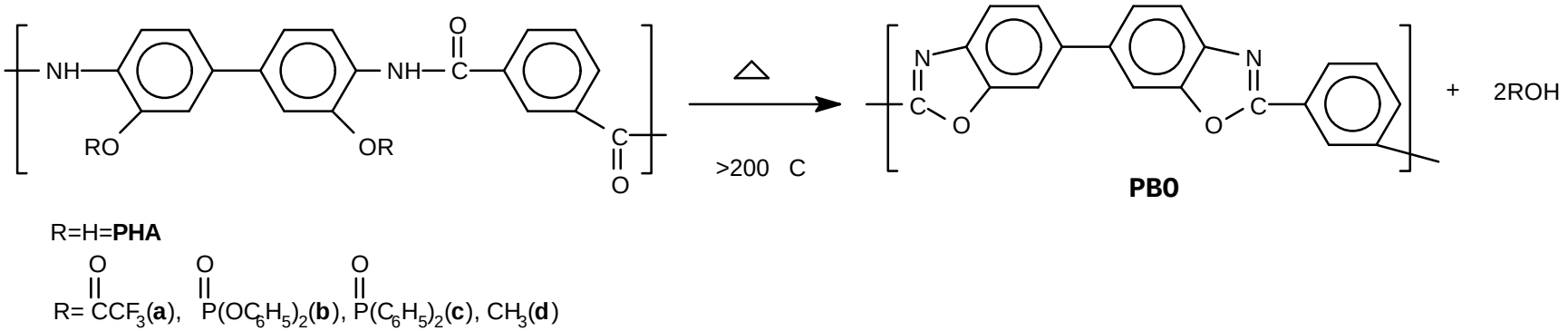

Scheme 1.