Deoxybenzoin-containing Polymers:
Combining Tailored Polymer Architecture with Non-halogenated Materials

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The widespread presence of synthetic polymers in modern society requires the discovery of mechanisms that reduce their inherent flammability, especially when considering confined spaces such as aircraft cabins. Flame retardant additives in use today are typically either inorganic or halogenated organic compounds, each with drawbacks that drive researchers towards alternative solutions. Our focus is on the synthesis of non-halogenated polymers that are inherently flame retardant despite having fully hydrocarbon structures. We have specifically focused on integrating deoxybenzoin and related structures into polymers, with advances in both stand-alone polymers and additives. Deoxybenzoin-based polymers exhibit impressive flame retardancy *via* char formation. For example, 4,4'-bishydroxydeoxybenzoin (BHDB) is an A_2 monomer that we prepare on a 200-gram scale by demethylation of desoxyanisoin. Polymerization of the deoxybenzoin monomer with different comonomers affords a variety of polymer types, including polyesters, polyphosphonates, polyurethanes, polysulfones, and cured epoxy networks. These deoxybenzoin-containing polymers exhibit exceptionally low heat release capacities (HRC) and total heat releases (THR), as measured by microscale combustion calorimetry (MCC), as well as high char residues. For example, deoxybenzoin-containing polyesters exhibit HRC values ≤ 100 J/g-K and char residues of >40%. Our recent investigations seek to combine control over polymer architecture with char mechanisms in polymer degradation. For example, modification of the deoxybenzoin monomer presents an opportunity to achieve highly branched or "hyperbranched" polymer architectures through the synthesis and polymerization of a deoxybenzoin-containing AB_2 monomer. This lecture will include detailed description of hyperbranched deoxybenzoin polymers by a one-pot synthesis as well as the spectroscopic and thermal characterization of the resultant polymers that characterizes their extent of branching. Notably, highly soluble branched deoxybenzoin polyesters were obtained from the novel deoxybenzoin AB_2 monomer and the resultant polymers exhibited very low HRC (133 J/g-K) and THR (12.6 kJ/g) values, and appreciably high char residue (42%). These branched polymers offer opportunities as polymer additives, blends, and coatings, all of which we are pursuing at present.