Hypervalent iodine(III) compounds in the synthesis of branched and functionalized polymers

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The potential of hypervalent (HV) iodine chemistry in organic synthesis has been well recognized but its versatility in materials science and polymer synthesis started gaining significant attention during the past decade. Cyclic HV iodine(III) compounds (benziodoxolones) with methacrylate- and acrylate-derived ligands were synthesized and characterized spectroscopically, by thermal analysis, and by single-crystal X-ray diffraction. Owing to the presence of a polymerizable moiety and an initiating site (the weak and homolytically cleavable HV I–O bond), the synthesized compounds can generate radicals upon irradiation with ultraviolet light, thereby serving as inimers in the synthesis of branched polymers through self-condensing vinyl polymerization. Copolymerizations with various monomers were performed under irradiation. This synthetic strategy circumvented the undesired crosslinking reactions that occur when (diacyloxyiodo)benzene-based compounds with polymerizable ligands are employed as inimers. In a different study, the ability of acyclic HV iodine(III) compounds with tetrazole, and fluorine-containing ligands to participate in functionalization reactions of cis-1,4-polyisoprene was explored. The results indicated successful modification, opening a new avenue to previously inaccessible functional and reactive polymers.