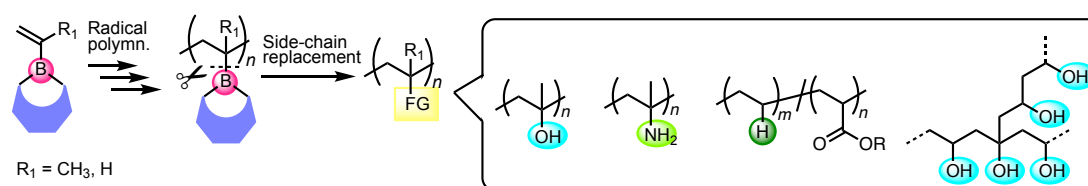


Alkenyl Boronates as a New Class of Vinyl Monomers for Tackling the Synthetic Limitations through Side-Chain Replacement in Polymer Reaction

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Keywords: Boron; Radical Polymerization; Post-Polymerization Transformation; Tacticity Control; Monomer Design

Chain-growth polymerization abilities of vinyl monomers are dependent on the element attaching to vinyl group. Therefore, there are numerous limitations in conventional vinyl polymer synthesis. If we find out novel vinyl monomers bearing replaceable side chains for introduction of various element on the main chain in polymer reaction through side chain replacement, it will enable breakthrough in conventional polymer synthesis toward flexible polymer design according to our wills. Boron is promising as the candidate of replaceable side chain with considering the emerging development of organic synthesis through carbon-boron bond transformation. Herein, radical (co)polymerization ability of alkenyl Boronates was discovered, and transformations of carbon-boron bond on the resulting polymers were performed for synthesis of conventionally inaccessible polymers through introduction of various element on the polymer backbone [1-8]. The vacant p-orbital of boron is the key to high radical (co)polymerization ability of boron monomers; moderate stabilization of chain growth radical by boron was essential for efficient chain growth reaction with suppressing side reactions. The introduction of various element (oxygen, nitrogen, proton) was possible through carbon-boron bond cleavage for synthesis of various polymers such as poly(α -methyl vinyl alcohol), poly(α -methyl vinyl amine), enthylene-acrylate copolymer, and branched poly(vinyl alcohol)s.



- [1] Nishikawa, T.; Ouchi, M. *Angew. Chem., Int. Ed.* **2019**, *58*, 12435. [2] Nishikawa, T.; Ouchi, M. *Chem. Lett.*, **2021**, *50*, 411. [3] Nishikawa, T.; Ouchi, M. *J. Synth. Org. Chem. Jpn.* **2023**, *8*, 313. [4] Makino, H.; Nishikawa, T.; Ouchi, M. *ACS Macro Lett.* **2020**, *9*, 788. [5] Makino, H.; Nishikawa, T.; Ouchi, M. *Chem. Commun.* **2021**, *57*, 7410. [6] Kanazawa, T.; Nishikawa, T.; Ouchi, M. *ASC Macro Lett.* **2022**, *11*, 706. [7] Suzuki, H.; Nishikawa, T.; Makino, H.; Ouchi, M. *Chem. Sci.* **2022**, *13*, 12703. [8] Makino, H.; Nishikawa, T.; Ouchi, M. *Chem. Commun.* **2022**, *58*, 11957.