Polymethacrylate Degradation Unlocked by Synergistic Dual Stimuli: Base Interaction and Photocatalysis on Boryl Pendants Leading to Main-Chain Scission

(*Graduate School of Engineering, Kyoto University*) ○Hiroshi Makino, Tsuyoshi Nishikawa, Makoto Ouchi

Keywords: Boron; Methacrylate Polymer; Photoreaction; Metal-free; Polymer Degradation

The development of degradable polymers collects increasing attention due to the social concerns about environmental pollution problems derived from remaining polymer debris for the long term. The incorporation of degradable trigger into the main chain is one of the typical approaches for making commodity polymers degradable. However, such triggers usually respond to a single stimulus, which could cause undesired degradation of the polymers in use. Therefore, the design of programmed degradation unlocked by synergistic dual stimuli should be useful for both stability and degradability.

Recently, we revealed that a boron pendant on the polymer main chain was usable as the trigger for the degradation of polymethacrylates via β-scission triggered by an excess amount of manganese oxidant in conjunction with a base.[1)] Given the recent progress in photocatalytic carbon-boron bond homolysis[2)], we came up with an idea that the boron trigger is available for programmed degradation by synergistic stimuli using photocatalysis. In this work, sodium methoxide (MeONa) was combined with 4CzIPN as a photocatalyst for backbone degradation of polymethacrylates under irradiation of blue light at room temperature (Figure 1). No degradation was observed in the absence of MeONa or photoirradiation, indicating that both base and photocatalyst were essential. Main-chain scission probably took place via photo-induced C–B bond homolysis of borates (boron-methoxide complex) and the subsequent β-scission. Thus, dual stimuli-induced degradation was achieved by taking advantage of the reactivity of boron.

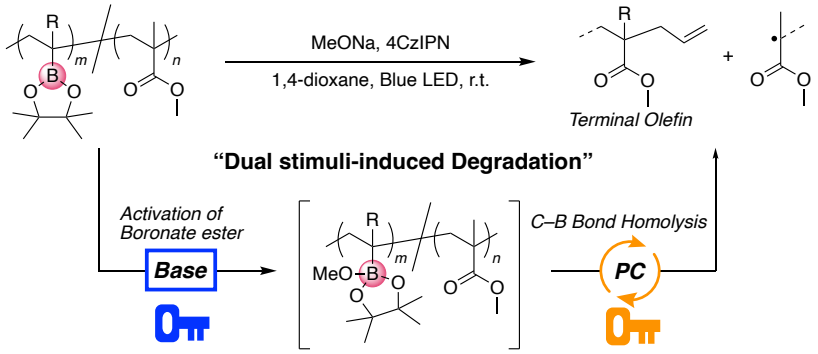

Figure 1. Synergistic dual stimuli-induced degradation of polymethacrylates bearing boronate esters.

1) Makino, H.; Nishikawa, T.; Ouchi, M. *Chem. Commun*. **2022**, 58, 11957.

2) Duret, G.; Quinlan, R.; Bisseret, P.; Blanchard, N. *Chem. Sci.* **2015**, 6, 5366.