Versatile Synthesis of Tacticity-Controlled PVA via Stereospecific Radical Polymerization of Vinylboronic Acid Derivatives

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Poly(vinyl alcohol) (PVA), a widely used synthetic polymer bearing hydroxy groups on the main chain, exhibits unique properties such as hydrophilicity and crystallinity. The tacticity is known to have a huge impact on the properties, and a considerable effort has been devoted for the stereoselective radical polymerization of vinyl acetate (VAc) and their derivatives, which are typical precursor monomers of PVAs.[1)] However, rigorous condition such as cryogenic temperature is needed for tacticity control, and thus the comprehensive control over the primary structures (e.g., tacticity and molecular weight) still remains challenging.

Recently, we revealed that radical (co)polymerization of alkenyl boronates and post-polymerization oxidation of boron pendant to synthesize various PVA derivatives.[2)] Given the tunable reactivity of organoboron compounds by boron protecting-group, we came up with exploration of the boron-protecting group design in vinylboron monomers for controlling the resultant polymer structure. In this work, we designed various monomers protected by anthranilamides bearing various alkyl groups on the nitrogen atom of the amide group toward synthesis of tacticity-controlled PVA via radical polymerization and subsequent oxidation (Figure 1). Consequently, tacticity of the obtained PVAs was dependent on the alkyl group: bulky alkyl substituents such as isobutyl and neopentyl groups afforded isotactic PVAs in contrast to small ones such as methyl and *n*-butyl leading to atactic tacticity. Interestingly, tetrahydrofurfuryl group-containing monomer allowed regulation of syndiotacticity. In the presentation, the mechanism of tacticity control and the stereospecific controlled polymerization for comprehensive structural control will be also described.

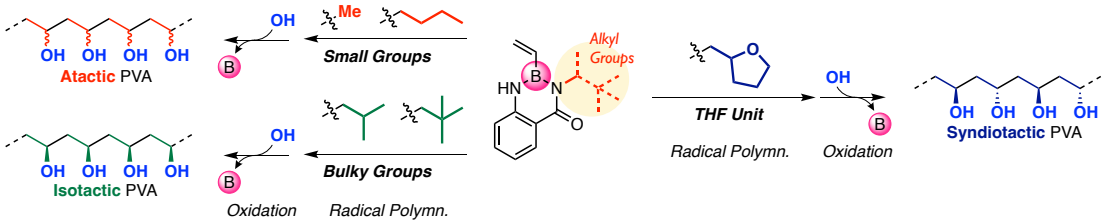

Figure 1. Design of protecting group in vinylboron monomers for syntheses of tacticity-controlled PVAs.

1) K. Satoh, M. Kamigaito, *Chem. Rev.* **2009**, *109*, 5120-5156. 2) T. Nishikawa, *Polym. J.*, **2024**, *56*, 873-886..