学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 目

Synthesis of 1,2-Glycosidic Polymers via Ring-Opening Condensation Polymerization of Cyclic Sulfite

（環状サルファイトの開環縮合重合による 1,2-グリコシド型ポリマーの合成）

Polysaccharide is a representative class of biopolymers, which consists of sugars with regularly-aligned stereogenic centers as a monomeric unit. The polysaccharide scaffolds are expected to be an indispensable motif for advanced functions such as chiral separation, asymmetric catalysis, and optical non-linearity. The synthetic studies of polysaccharides have been extensively investigated to disclose several fruitful methods for a part of polysaccharides including (1→3), (1→4), and (1→6)-linked polysaccharides.

Recently, the author became intrigued by the remaining (1→2)-glycosidic polymers. (1→2)-β-Glucopyranan is a natural polysaccharide, isolated from *Agrobacterium* and *Sinorhizobium* genera to cause crown gall disease of plants. The bacterium exhibits nitrogen gas-fixing ability to provide ammonia to the plants. It is invoked that the polymer would play an important role to interact between the bacterium and the plant host, although the interaction mechanism has not been systematically unveiled. The polymer has glucose repeating units linked together by (1→2)-glycosidic bonds, which forms a rigid helical structure bearing side-chain hydroxyl groups that may be useful in molecular integration. It has been also reported that natural glycosides bearing (1→2)-linked oligosaccharides, such as glycyrrhizin, cyaniding-3-*O*-sophoroside, and quercetin-3-*O*-sophoroside, exhibit unique bioactivity. The synthesis for the (1→2)-linked polysaccharide has been realized only via cationic polymerization of an unstable epoxide monomer, which led the polymer to a broad polydispersity index. The syntheses of the oligosaccharide-containing glycosides were mainly based on the stepwise glycosidations, which required time-consuming multi-step reactions and purification processes.

This thesis focuses on the development of new synthetic method for 1,2-glycosidic polymers via ring-opening condensation polymerization of a sugar-based cyclic sulfite. I found that cationic polymerization of the cyclic sulfite afforded (1→2)-D-glycopyranan along with the elimination of SO_2. The polymerization enables reliable preparation of (1→2)-linked glycosidic polymers with a narrow polydispersity index and the introduction of glycosylation-active pentenoly group to the polymer terminus. The method was also applied to both grafting-onto and grafting-from polymerizations to give the corresponding glycosides.

In chapter 1, the author described the general backgrounds of polysaccharides and glycosides.

Polysaccharides are divided into four classes based on the glycosidic position. The structural features and synthetic methods for each class were systematically described. Through the historical survey, the importance on the synthetic studies of 1,2-glycosidic polymers was particularly emphasized.

In chapter 2, the author discussed the chemical stability and reactivity of cyclic sulfite as a monomer, mainly by the comparison with those of glycal epoxide as a conventional monomer. Kinetic studies for the degradations evaluated the higher stability of the cyclic sulfite than the epoxide. At first, the anionic ring-opening polymerization of cyclic sulfite was investigated by using potassium *p*-tolylthiolate (*p*-TolSK) as an initiator in DMF, according to the model studies of nucleophilic substitution to the cyclic sulfite. However, it was indicated that the anionic polymerization was unfruitful, which gave an inseparable mixture of the polymer and some other impurities containing sulfur.

In chapter 3, the author described the cationic polymerization of the sugar-based cyclic sulfite. The polymerization was performed by using 4-penten-1-ol as an initiator in the presence of trifluoromethanesulfonic acid (TfOH) and MS 3A in CH_2Cl_2. From the spectroscopic analyses of the obtained polymers, it was found that the cationic polymerization of cyclic sulfite efficiently eliminates SO_2 to form the corresponding 1,2-glycosidic polymers bearing a pentenoyl group at the polymer terminus. The distributions of the polymers were narrower than those of the previous polymers prepared from an epoxide monomer. The anomeric stereochemistry of the polymers was moderately controllable by changing the reaction temperature. The effects of the monomer structures on the polymerization of cyclic sulfite were also investigated through a comparison between the results of glucose and galactose derivatives. As an application, the author demonstrated the glycosylation reaction using the terminal pentenoyl group. The grafting reaction would provide a promising pathway for the creation of polysaccharide-containing graft copolymers and the cyclic polymers in the future.

In chapter 4, the author described the new grafting reaction using cyclic sulfite from glycyrrhitic acid to give glycyrrhitic acid polyglycosides in one-pot. The reaction enables the rapid preparation of glycyrrhizin derivatives consisting of oligosaccharides with arbitrary polymerization degree.

Chapter 5 is the general conclusion. Chapters 2-4 clearly shows the usefulness of the sugar-based cyclic sulfite as a new monomer for 1,2-glycosidic polymers. The present results provide new insights into not only natural product syntheses but also the creation of high performance polymers based on a grafting reaction.