Title	ユニークな桂皮酸二量体を用いた高性能ポリマーの分子設計
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Abstract

For upcoming the sustainable society, the development of high-performance/functional biobased polymer materials has attracted interest from researchers. Cinnamoyl photodimers, which are derived from cinnamic acids by photo-assisted [2+2] cycloaddition, have high potentials to be used as monomers for the high-performance/functional polymers due to structural characteristics such as rigid structure, unique bending angles, chirality, and photodegradable cyclobutane. However, though cinnamoyl dimers have many interesting properties, only a few cinnamoyl dimer-based polymers were reported and the effects of cinnamoyl dimer moiety on the corresponding properties of polymers are not clear enough. In this thesis, the author describes effects of cinnamoyl dimer unit in polymer backbone on polymer properties through the developments of high-performance/functional polymers from unique cinnamoyl dimers.

This thesis is composed of following five chapters:

Chapter 1 describes the background and objectives of this research.

Chapter 2 describes the synthesis of mussel-mimetic photodegradable adhesive materials from 3,4-dihydroxycinnamoyl dimer (34THTA). The 34THTA was synthesized from 3,4-dihydroxycinnamate by solid-state photodimerization and then was polymerized to synthesize polyamides bearing adhesive catechol groups in the side chain. As a result, obtained copolyamide exhibited good adhesive properties of ~7 MPa for stainless steel substrate. In addition, the cyclobutanes in polymer backbone were cleaved by ultraviolet light irradiation. The results described in this chapter provide insights into the molecular design of eco-friendly, high-performance adhesive materials with photodegradability.

Chapter 3 describes the selective synthesis and polymerization of *β*-, and *δ*-type 4-aminocinnamoyl photodimers. In the solid-state photodimerization of 4-aminocinnamic acid derivatives, selective synthesis of each isomeric dimers was achieved by controlling molecular arrangements in the crystal. Density functional theory (DFT) calculations revealed that the *β*- and *δ*-type photodimers possessed unique bending angles of 70° and 101°, respectively. In addition, each obtained dimers were modified to diamine and dicarboxylic acid monomers then was used for the synthesis of polyamides. The present study provides a synthetic method for isomeric 4-aminocinnamoyl dimers, which have potential for high-performance and/or functional polymers based on the unique cinnamoyl dimer skeleton.

Chapter 4 describes the synthesis of soluble biobased polyimides from isomeric 4-aminocinnamoyl photodimer-based diamines with unique bending angles. The *β*-, and *δ*-type diamines, which were synthesized in chapter 3, were polymerized with tetracarboxylic acid dianhydrides to produce soluble polyimides. As a result, *δ*-type dimer-based polyimides exhibited high thermostability and good solubility in organic solvents such as chloroform owing to its rigid and bending structure. The results described in this chapter showed the diamine with an angle of 101°, similar to *δ*-type, had a suitable structure to provide solubility to the obtained polyimides. The present study provides insights into the molecular design of high-performance soluble polymers by focusing on the bending angles of the polymer chains.

Chapter 5 summarizes the syntheses and evaluation of high-performance/functional polymers using unique cinnamoyl dimers as the overall conclusions of this thesis. This research is mainly focused on the effects of cyclobutane rings in polymer backbone. since the cyclobutane rings are easily obtained by [2+2] cycloaddition of olefins, the obtained insights would be possible to expand other polymer systems including olefin structures.

Keywords: Biobased polymers, Polyamide, Polyimide, Cinnamic acid, Photodimerization, Cyclobutane.