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Ultrahigh heat-resistant, transparent bioplastics from exotic amino acid

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Abstract

Most cinnamate derivatives were biosynthesized via sikimate pathway in plants and bacteria, and the cinnamates were used as renewable starting materials for high-performance polyesters. *p*-hydroxycinnamic acid (4HCA), ferulic acid (MHCA), caffeic acid (DHCA), 4-aminocinnamic acid (4ACA) were selected as bioresources. As a result of investigating the structure-property relationships of polyesters from these hydroxyacids, we found that poly(4HCA-*co*-DHCA)s showed high mechanical strength, high Young's modulus, and high softening temperature. However thermal degradation temperature of the polyesters was limited to around 300 ^{o}C, which restricts the application. Then we used an exotic amino acid, 4ACA, which was bioavailable by microorganism engineering. The photodimer of 4ACA was used as a bio-based monomers for aromatic polyamides and polyimides. Especially the polyimides derived from the photodimer and cyclobutanetetracarboxylic dianhydrides showed a good thermomechanical performance, a high transparency, and high breakdown voltage as in insulators. These mechanical performances are higher than those of conventional transparent polymers, in spite of limited molecular design by bio-based molecules.

Selection and Peer-review under responsibility of Conference Committee Members of 5th International Conference on Functional Materials & Devices (ICFMD 2015).

Keywords: Bioplastics; Polyimides; Polyesters; Cinnamoyls; Transparent materials

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1. Introduction

Renewable bio-based polyesters are indispensable for establishing the green sustainable society [1]. However, some aliphatic bio-based polyesters, such as poly(hydroxyalkanoate)s [2], poly(butylene succinate) [3], and so on [4], did not show performances high enough to apply in engineering plastic fields. Improvements in durability and performance have been shown by Ecoflex^{TM} [5] and Biomax^{TM} [6], but environmental toxicity and availability of terephthalic acid are problematic. Poly(lactic acid)s (PLA) have been remarkably well developed because of their high mechanical strength [7]. However, it was estimated that these polyesters will only replace a small percentage of nondegradable plastics currently in use due to their poor level of thermoresistance. As a result, high performance environmentally-friendly polymers originally from and degradable into natural molecules are earnestly desired for improving human life. Many nondegradable engineering plastics have rigid conjugated rings, such as benzene, benzimide, benzoxazole, benzimidazole, or benzthiazole [8]. The introduction of an aromatic component into a thermoplastic polymer backbone is an efficient method for intrinsically improving material performance [9]. Additionally, the continuous sequence of aromatic rings can be a mesogenic group. Moulding in the thermotropic liquid crystalline (LC) state can induce molecular orientation giving anisotropy to the mechanical performance, which sometimes dramatically increases mechanical strength and Young's modulus [10]. In this review, we discuss the preparation of various rigid polymers derived mainly from phytochemical monomers [11]. We have selected cinnamates as aromatic phytomonomers since their rigidity and photoreactivity can lead to high heat-resistance and photofunctions of corresponding polymers. Hydroxycinnamates can be used as monomers for high thermoresistance polyarylates. Additionally we have used the photodimer of a microorganism-derived aromatic monoamine, 4-aminocinnamic acid (4ACA), to prepare bio-derived polyimides (PIs) based on its reaction with various tetracarboxylic dianhydrides, and obtained high performance polyimides with high thermomechanical properties, high transparency, and good cell-compatibility.

2. Bio-based polyarylates

2.1. Biomonomers

One of the most famous coumarates is *p*-coumaric acid (4-hydroxycinnamic acid; 4HCA). In fact, lignin biosynthesis starts with conversion into cinnamate and 4HCA via the enzymatic reaction with phenylalanine ammonia lyase and Cyt P450-dependent monooxygenase, respectively [12]. 4HCA derivatives are used as allelopathic chemicals in plants and widely exist in soil [13]. 4HCA is also available in several photosynthetic bacteria as a protein component [14-16]. *Rhodobacter capsulates* [14], *Rhodobacter sphaeroides* [15], and so on [16] contain photoactive proteins comprised of a photosensitive 4HCA component. Light irradiation (λ=375 or 435 nm) results in an E-Z transformation that enables bacteria to swim away from the light. Furthermore, since the enzymatic conversion of amino acids to phytomonomers is well defined and straightforward, scale-up for mass-production is feasible [17]. These phytomonomers were biodegraded by microbial action [18]. Ferulic acid (3-methoxy-4-hydroxycinnamic acid; MHCA), and caffeic acid (3,4-dihydroxycinnamic acid; DHCA), have also been selected as phytomonomers, since these molecules are widely available in various plants with an essential pathway of lignin biosynthesis [12]. We also

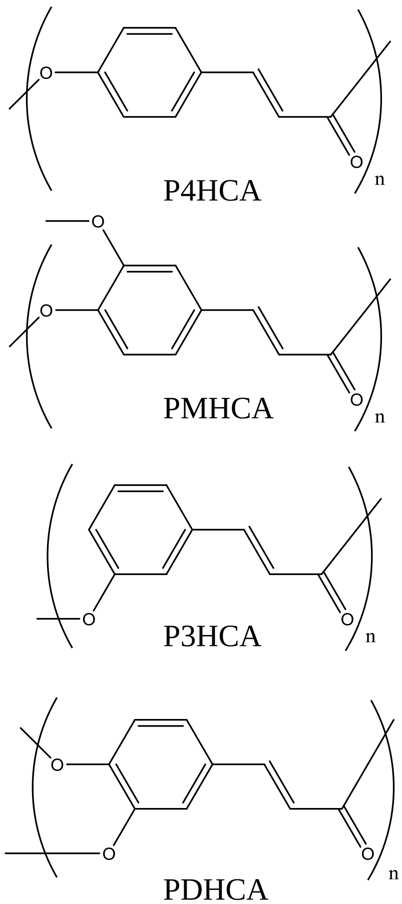

Fig.1. Structures of polyarylates derived from bio-based hydroxycinnamic acid.