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Title	４－アミノ桂皮酸二量体をモノマーとするバイオベースポリアミド／イミドの合成
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Abstract

Due to limitation of oil-field and hence petroleum-derived products, bio-based materials are indispensable in low-carbonation society establishment. Super engineering plastics from biomolecules are suitable for the materials in terms of available amount and cost. The development of these high performance bio-based polymers is crucial to establish sustainable low-carbon society. The syntheses of high performance bio-based polymer including polyamide and polyimides (PI)s with photofunction properties derived from bioavaiblable starting material was the uttermost focus of this research.

The bio-based monomers of polyamide and polyimide such as diamine and diacid were synthesized along with the synthesis of total bio-based polyamide. The detailed syntheses are discussed in Chapter 2. New route for the synthesis of monomer diamines 4,4'-diaminostilbene (DAS), 4,4'-(ethane-1,2-diyl)dianiline (EDDA) and diacid N,N'-diacetyl-4,4'-diamino-α-truxillic acid (DADTA) from bio-derived 4ACA was explored. The prepared monomers were characterized using ^{1}H NMR and ^{13}C NMR. A novel diamine i.e. 3,6-bis(4-aminobenzyl) piperazine-2,5-dione (BAPD) was prepared by a series of chemical modification starting with 4-aminophenylalanine (4APhe) by optimizing each step and the synthesis route was established. The prepared diamine DAS and diacid DADTA were employed to react in presence of TTP in DMAc to form total bio-based polyamide which was characterized by FT-IR, GPC and TGA. From TGA it was observed that the polyamide showed high T_{d10} at 367 °C.

In Chapter 3, fully bio-based and semi-bio-based PIs were synthesized and characterized w.r.t their thermal and mechanical properties. DAS and EDDA were synthesized from bioavailable molecule via Grubb's coupling reaction. PAAs were synthesized by condensation polymerization of DAS with dianhydrides (yields: 90-98%). PAA films were prepared by spin-coating which were then thermally imidized to prepare PIs film. Molecular weights ranged 2.2 x 10^5 – 4.0 x10^5 g/mol for M_w. Inherent viscosities ranged 0.41-6.62 dl/g (PAA-1f highest). PIs showed high degradation temperatures of T10 ranging 500-600 ^{o}C. The tensile strength of PI-1f$^{\#\#}$ was found to be 132 MPa higher than that of Kapton^{TM}. Thus every biopolyimide prepared here showed high thermal and mechanical properties. The effect of various factors such as polymerization time and mixture of dianhydride were carried out. As per GPC the 32 h polymerization time was found to be good, however, 24 h polyimides gave good thermal and mechanical properties. The polyimide from mixture of dianhydride posses the properties lying from the polyimide from pure dianhydride.

Chapter 4 deals with the photo-functional properties of PAAs and PIs. All the PAAs synthesized from amine DAS were found to be UV-vis active and the fluorescence studies revealed the effect of UV-vis irradiation on PAAs. UV-vis irradiation was found to control the fluorescence intensity due to the crosslinking of PAA chains which was proved by ^{1}H-NMR hence UV-vis irradiation can help in modifying the polymers fluorescence properties to the desired one. The crosslinking and inter conversion of *trans* to *cis* to cyclobutane was proposed and confirmed.

KEYWORDS: stilbenes, polyimides, high performances, photofunctions, aromatic diamines.