Abstract of Doctoral Dissertation

Studies on functional bio-based polymers from aromatic amine derivatives

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The development of bio-based functional polymers is significant for the establishment of a sustainable low-carbon society. Although various bio-based polymers have been developed, almost all of them were aliphatic polyesters which generally have no specific function. In this respect, these aliphatic bio-based polyesters can be used in the category of commodity plastics, but the widespread use of bio-based polymers is very difficult to achieve given the severe competition with the commodity plastics currently in use. The functionalization of bio-based polymers is very important for applications in advanced fields.

From this concept, bio-based plastics having a performance high enough to use as variety of functional plastics would be highly suitable. The introduction of an aromatic component into a thermoplastic polymer backbone is an efficient method of intrinsically improving material performance. For example, poly(*p*-phenylene-2,6-benzobisoxazole) (PBO) exhibited ultrahigh strength/high modulus properties because they had a rigid-rod structure to exhibit liquid crystal phase. The polymer is able to obtain from 3-amino-4-hydroxybenzoic acid (3,4-AHBA) derived from microorganism *Streptomyces griseus* as a precursor for several secondary metabolites. 3,4-AHBA is a renewable, functional benzene derivative with three substituents of amino, carboxyl, and hydroxyl groups. Here the author prepared a couple of environmentally friendly, functional polymers such as (1) π-conjugated conductive polymer, (2) liquid crystalline copolymer, and (3) novel π-conjugated PBO using a bioderived resource 3,4-AHBA in order to contribute the establishment of sustainable low-carbon society as follows

(1) 3,4-AHBA contains aniline in the structure. In this meaning, π-conjugated polyaniline derivative, P(3,4-AHBA) was prepared by electropolymerization method. P(3,4-AHBA) has higher solubility in various polar solvents ,compared to polyaniline, due to the side groups of carboxyl and hydroxyl. The polymer also showed unique properties such as solvatochromism and halochromism, and gave a flexible film with a conductivity as high as that of semiconductor.

(2) 3,4-AHBA has two functional groups such as hydroxyl and carboxyl, and it could be applied for polyester with aniline moiety. Here the author prepared the thermotropic liquid-crystalline copolymer, poly{3-benzylidene amino-4-hydroxybenzoic acid (3,4-BAHBA)-*co*-*trans*-4-hydroxycinnamic acid (4HCA)} (P(3,4-BAHBA-*co*-4HCA)) by a thermal polycondensation of 3,4-BAHBA and 4HCA which is one kind of phenolic biomonomer. The copolymers showed liquid crystalline phase, and the oriented films of the copolymers showed polarized fluorescence properties.

(3) 3,4-AHBA could oxidize amine to nitro group, and reduce carboxyl to get aldehyde compound 3-nitro-4-hydroxy benzaldehyde (3,4-NHBAL). By using 3,4-NHBAL, it could easily react with amine such as hydrazine to get symmetric compound. Here the author prepared novel aromatic symmetric precursor, poly(hydroxyl amide) by starting from 3,4-NHBAL and the stepwise cyclization from precursor to PBO under different thermal conditions. PBO precursors showed good solubility, and its film converted to PBO by heating.

In conclusion, the author designed new π-conjugated polymer systems from 3,4-AHBA as a renewable resource. It could play an important role to replace not only petroleum-based polymers but also apply for liquid crystalline materials, photo functional advanced materials, and engineering plastic materials.

Key words: bio-based functional polymer, 3-amino-4-hydroxybenzoic acid, polyaniline derivative, liquid crystalline polymer, PBO.