

Title	高性能バイオベースポリベンズイミダゾールの合成とそれらの電気的応用
Author(s)	Nag, Aniruddha
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Description	Supervisor:金子 達雄

Syntheses of High Performance Bio-based Polybenzimidazoles and their Electrical Applications

Abstract

Due to limitation of petroleum-based resources, bio-based materials are important to establish sustainable society. Research in this thesis described the syntheses of high-performance polybenzimidazoles using biomass and various applications depending on their structure-property relationships.

In chapter 2, various monomer syntheses were described such as; 3-amino-4-hydroxybenzoic acid (3, 4-AHBA) using *Streptomyces sp.* and also 3, 4-diaminobenzoic acid (3, 4-DABA) was prepared using chemical conversion of aromatic hydroxyl into aromatic amine starting from 3, 4-AHBA. Each step was optimized and detailed synthetic procedures were described along with their ^1H and ^{13}C -NMR characterizations. Another monomer *p*-aminobenzoic acid (PABA) was also introduced which can be derived using biomass. Furthermore, in this chapter we have described homopolymer preparations of poly(2, 5-benzoxazole) (PBI) using 3, 4-AHBA and poly(2, 5-benzimidazole) (PBO) using 3, 4-DABA. Those structures were characterized using FT-IR and solid-state NMR analysis. Thermal stability of the aforesaid polymers were found with 10% weight-loss temperatures (T_{d10}) of 622 °C and 700 °C for PBO and PBI respectively, which are enough high comparable with super-engineering plastics and even higher than few of the metals. Mechanical analysis was also performed and tensile strength of PBI and PBO copolymers were found to be 75 MPa and 53 MPa with Young's modulus values of 3.6 and 2.8 GPa respectively.

In chapter 3, author focused on various copolymer syntheses using bio-based monomers. Both PBI and PBO homopolymers are very reluctant to get soluble in any of the conventional solvents due to their rigid ring structures, thus flexible chain was introduced with PBI moiety using PABA homopolymer to prepare PBI-*co*-PA (PBI-*co*-PA). PBO homopolymer was found to have high thermo-mechanical stability and superior insulating properties (low dielectric constant, high resistivity etc.) comparable with commercial dielectric materials. On the contrary, PBI homopolymer was already established with ultra-high thermal stability but consisting of conducting imidazole proton. After considering, another series of novel copolymer PBO-*co*-PBIs were made to control balance between thermo-mechanical stability and insulating properties. PBI-*co*-PA with very low amount of PA incorporation showed highest thermal stability ($T_{d10}= 743^\circ\text{C}$) among all the existing polymers in the world so far, and they can be used to prepare hybrid materials with metals at a temperature over the melting temperatures of the metals. Another copolymer PBO-*co*-PBI shows dielectric constant very low ($\epsilon_r=2.0$) when consist of higher PBO content and the values are comparable with commercial ultra-low k materials such as; PE or PP.

In chapter 4, research focus was shifted towards structure modification of the prepared bio-based polybenzimidazoles for specific application. It was reported by many other groups that, imidazole proton on PBI polymer chain can be substituted with alkyl chains, metals etc. But for the first time we have prepared organoborane moiety by substituting PBI imidazole protons and tried to incorporate conducting lithium ion loosely bound to the polymer chain. Modified PBI structure was further hybridized with different amount of ionic liquid BMImTFSI to prepare various pseudo solid polymer electrolyte and application of those in secondary Li-ion battery were also checked. Due to innovative molecular designing ultra-high ionic conductivity was observed ($\sim 10^{-2}$ S cm⁻¹) even higher than most of the reported solid polymer electrolytes so far. Anodic half-cell produced higher discharge capacity of 1300 mAh g⁻¹ and stable coulombic efficiency for long cycling. Also, comparatively new technique of interfacial study (dynamic electrochemical impedance spectroscopy, DEIS) was performed to check the solid electrolyte interface (SEI) layer stability.

Hence, in this research theme, we have successfully synthesized various high-performance benzazole polymers using bio-derived and bio-based monomers, which are comparable with engineering grade plastics. Also, copolymerization between various bio-based monomers and depending upon their structural compatibility various properties were established. Side chain modification of the polymer was done for specific applications such as; pseudo-solid polymer electrolyte in Li-ion battery.

Keywords: polybenzimidazole, polybenzoxazole, copolymer, dielectric, conductivity, Li-ion battery