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論　　文　　題　　目	Syntheses of High-Performance Bio-based Polybenzimidazoles and their Electrical Applications
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論文の内容の要旨

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 ^{1}H 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°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 (ε_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 (~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

論文審査の結果の要旨

バイオプラスチックの重要性は年々高まってきている。一方、その耐熱温度などの性能は低く機能にも乏しい。本論文では、放線菌が生産する芳香族アミノ酸で遺伝子組み換え大腸菌により大量生産可能な３－アミノ－４－ヒドロキシ安息香酸を題材にポリベンズイミダゾールおよびその誘導体を合成し、高い熱的・力学的物性のフィルムを与える分子設計を行い、かつイオン電導性などの機能を与えることを目的として研究を進め、以下のように纏めた。

第一章では、バイオプラスチック、高性能分子の合成論と応用、芳香族アミノ酸に関する研究背景を述べ、従来報告されてきた論文をレビューすることで、本論文の位置づけを行い、目的、

意義を述べた。

第二章では、３－アミノ－４－ヒドロキシ安息香酸を出発物質とし、ポリベンズイミダゾールのモノマーである３，４－ジアミノ安息香酸への変換ルートを構築した。また、３，４－ジアミノ安息香酸の重合によりフィルム化の可能なポリベンズイミダゾールが合成できることを明らかにした。

第三章では、前章のポリベンズイミダゾールを基盤として４－アミノ安息香酸を共モノマーとするアラミド共重合体や３－アミノ－４－ヒドロキシ安息香酸を共モノマーとするポリベンズオキサゾールとの共重合性を確認した。その結果、いずれの系においても共重合性は大変良く、あらゆる組成比の共重合体が得られることが分かった。特に、ポリベンズイミダゾール/アラミド共重合体で 15%のアラミド成分が導入されたものに関しては、全てのポリマーの中で最も高い熱分解温度（10%重量減少温度：743℃）を示すポリマーを合成するに至った。

第四章では、第二章で合成したポリベンズイミダゾールの誘導体化のためにトリエチルボランによる修飾を行った。その結果、リチウムイオンを対イオンとするトリエチルホウ素化ベンズイミダゾレートアニオンを導入することに成功した。続いて、得られた誘導体の粉末をイオン液体により可塑化することで、極めて高いリチウムイオン伝導性を示す擬固体高分子電解質を作成することに成功した。この電解質を含む半電池を作製し充放電特性などを確認した結果、極めて高いイオン伝導度、広い電位窓を有することに加えて 30 回の充放電サイクルに耐える高性能な電解質であることが見いだされた。

第五章では、全ての章を総括し、当該ポリベンズイミダゾール誘導体の構造物性相関を纏めて説明した。以上、本論文は最も高い耐熱性のプラスチックフィルムや高性能なリチウムイオン伝導性擬固体電解質を初めて設計・合成し、かつ構造機能相関を明確にするなど学術的に貢献するところが大きい。よって博士（マテリアルサイエンス）の学位論文として十分価値あるものと認めた。