Title	超高耐熱性と誘電性能を示す芳香族バイオポリベンザゾールの開発
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ABSTRACT

Bio-materials are of great significance for sustainable development of society due to the restriction of fossil fuel-based resources. Tremendous efforts have been focusing on developing bio-based materials have comparable performance with fossil fuel-based materials. Work in this thesis described the syntheses and characterizations of bio-based polybenzazoles with high thermal resistance and dielectric performance.

In chapter 2, conventional 2,5-polybenzoxazole and new 2,6-polybenzoxazole were synthesized from bioderived 3-animino-4-hydroxylbenzoic acid and 4-amino-3-hydroxylbenzoic acid respectively. There is no significant difference between there thermal resistance in homopolymer state. However, after copolymerized with polybenzimidazole, in the same molar composition, 2,6-polybenzoxazole-*co*-polybenzimidazole presents an obvious higher thermal decomposition temperature than 2,5-polybenzoxazole-*co*-polybenzimidazole, the highest 10% mass loss temperature reaches 740 °C, the obtained copolymer can be used to fabricate pliable film, suggesting this copolymer is promising to be utilized as thermoresistant materials.

In chapter 3, polybenzothiazole was synthesized from bio-based resources for the first time. The precursor monomer 4-amino-3-mercaptobenzoic acid was synthesized from bio-derived 4-aminobenzoic acid, and the obtained monomer was copolymerized with PBI and obtained a series of copolymers. The thermoresistance and dielectric properties were characterized. The copolymer presents an increasing thermal stability as increasing the amount of PBI, this is probably due to existence of hydrogen bond elevated the thermal stability. Besides, polybenzothialzole-co-polybenzimidazole presents dielectric around 3, lower than most of the dielectric polymers. This is probably due to the low-polar structure of thiazoles, enhanced the dielectric performance of the copolymers.

In chapter 4, terpolymer poly{benzimidazole-*b*-(benzoxazole-*r*-amide)} with a block structure was synthesized with a stepwise terpolymerization of 3 monomers. The obtained terpolymers present ultrahigh thermal resistance, and the thermoresistance increases with the increasing molar compositions of polyamide, the mechanism of this was revealed by DFT calculation, the result indicate that the appropriate amount incorporation of polyamide can impede the resonance effect and thus increase the molecular interaction enthalpy, as a result, the thermal stability is enhanced, the high thermoresistance is attributed to the hydrogen bonds. Besides, the dielectric constant of the terpolymers vary within 2.4 to 3, showing an outstanding dielectric performance. Considering the high performance in both thermal and dielectric properties, the terpolymer was successfully utilized as a coating material for copper coil, indicating the terpolymer is promising to be used as thermostable insulating materials.

In conclusion, polybenzazoles having ultrahigh thermal stability were designed and synthesized bio derived resources. The obtained polymers exhibit outstanding performance in mechanical and dielectric properties besides thermal resistance, making them promising to be utilized as high-performance thermal dielectric material. The successful synthesis of polybenzazoles from bio resources provides an approach to offset the negative influence of the depletion of petroleum resources. The exploration of hydrogen bond interaction enthalpy revealed the impact of H-bond on thermal stability and this can be of great significance for the chemical design and construction of polymers.

Keywords: polybenzazoles, thermoresistance, low-k, copolymer, H-bond