報告番号	※甲　　第　　号

主　論　文　の　要　旨

論文題目　Synthesis of 3-Arylsuccinimides and Polyimides by Brønsted Acid-Catalyzed 1,4-Additions
（ブレンステッド酸触媒による 1,4-付加反応を基軸とした 3-アリールスクシンイミドおよびポリイミドの合成）

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論　文　内　容　の　要　旨

3-Arylsuccinimides have a wide range of potential applications in pharmaceutical industries and academic communities. A remarkable example is *N*-methyl 3-phenylsuccinimide, known as an anticonvulsant drug under the trade name Milontin. 3-Arylsuccinimides are also important as synthetic intermediates for heterocyclic compounds such as ω-carbinol lactams, pyrroles, pyrrolidines, and maleimides. These applications have prompted researchers to develop a number of synthetic methods for 3-arylsuccinimides. Most of the reported methods employed metals as promoters or catalysts, which may not be removed from the product. Use of metals should be avoided if possible. From this point of view, two metal-free methods have been developed, but the substrate scope was limited.

First, 1,4-addition of 1,3,5-trimethoxybenzene (TMB) to *N*-methylmaleimide was used as a model reaction for the optimization of conditions. Screening of several Brønsted acids in different solvents revealed that a combination of trifluoromethanesulfonic acid (TfOH) in a low polar solvent such as toluene or 1,2-dichloroethane (DCE) under heating conditions showed the highest reactivity. The conditions were applicable to the synthesis of various 3-arylsuccinimides. A good functional tolerance was observed for unprotected maleimide, hydroxy, and carboxyl groups. In reactions with *N*-arylmaleimides, the products were isolated without tedious column chromatography. The reaction was conducted on a gram scale with excellent yields.

Next, the reaction conditions with a slight modification were applied to the synthesis of 3-arylpropionic acids and its esters. At room temperature, TMB was successfully added to acrylic acid, its esters, itaconic anhydride, and 2-hydroxyethyl methacrylate to afford the corresponding 1,4-adducts. The results revealed that α-substituted acrylates with a five-membered cyclic

structure have no effect on reactivity.

Finally, the newly developed 1,4-addition reaction was applied to the synthesis of novel polyimides from bismaleimides and 1,3-bis(3,5-dimethoxyphenoxy)propane. The optimization of the reaction revealed that *m*-cresol was the solvent of choice and that the resulting polyimide was obtained with a number average molecular weight (M_n) and a molar-mass dispersity ($Đ_M$) of 8000 and 2.2, respectively. The structure of the polymer was characterized by ^{1}H NMR, two-dimensional NMR, and MALDI-TOF MS measurements. Moreover, both linear and cyclic polymers were formed with a mixture of regioisomers on the benzene rings. Replacement of 1,3-bis(3,5-dimethoxyphenoxy)propane with 5,5'-oxybis(1,3-dimethoxybenzene) gave polymers with smaller M_n values of approximately 4000. The polymerization results indicated that the aliphatic backbone structure of the nucleophilic monomer could affect the degree of polymerization significantly. The new methoxybenzene-linked polyimides are potentially thermostable: their 10% weight loss temperatures (T_{d10}) are in the range of 422 to 441 °C and their glass transition temperatures (T_g) are around 200 °C. These polymers are soluble in various organic solvents such as *m*-cresol, DMF, and chloroform, offering benefits for processing. The study provides a new polymerization method and polyimides containing alkoxybenzenes, which are similar to components of lignin. Therefore, the resulting polymers are expected to show biodegradability.

In conclusion, novel TfOH-catalyzed 1,4-additions of 1,3,5-trimethoxybenzene to maleimides and acrylates with good functional tolerance were developed. The method provides a new series of 3-arylsuccinimides and 3-arylpropionic acid derivatives. The reaction was also applied successfully to the synthesis of new polyimides with high thermal stability and good solubility. The biological activities and physical properties of the new compounds obtained in this study should be investigated in the fields of biology and polymer science.