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題目(和文)	C-H官能基化を経る遷移金属触媒重縮合による全芳香族ポリマーの合成
Title(English)	Synthesis of Wholly Aromatic Polymers by Transition Metal-Catalyzed Polycondensation Through C-H Functionalization Process
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種別(和文)	要約
Type(English)	Outline

On the basis of directing group assisted C-H functionalizations, the author has described new transition metal-catalyzed polycondensation systems that involve C-H functionalization processes and the synthesis of various wholly aromatic polymers on the basis of these polycondensation methods. This thesis consists of 5 chapters, and the outline for each chapter is shown as follows.

In **Chapter 1**, the research background related to the synthesis of wholly aromatic polymers including π-conjugated polymers, and the C-H functionalization reactions and polycondensations is described.

In **Chapter 2**, the polycondensation of 4,5-dihydro-2-phenyloxazole and aryl dihalides via the Ru-catalyzed C-H functionalization is described. The polycondensation was carried out to produce the wholly aromatic polymers in high yields whose number-average molecular weights reached to 20000. It was found that the addition of pivalic acid to the polymerization system facilitated this polycondensation leading to the production of polymers with higher molecular weights.

In **Chapter 3**, the polycondensation of phenylpyridine derivatives and aryl dihalides through the C-H functionalization process and the synthesis of wholly aromatic polymers based on this synthetic method is described. In **Section 1**, the polycondensation of 2-phenylpyridine and aryl dihalides via the Ru-catalyzed C-H functionalization was carried out to produce wholly aromatic polymers in high yields. Wholly aromatic polymers consisting of meta-phenylene linkages were also obtained by the use of various aryl dihalides.

In **Section 2**, the Ru-catalyzed direct double arylation of 1,4-bis(3-methylpyridin-2-yl)benzene with bromobenzene (2.0 equiv) proved to take place in a 2,5-specific fashion to give a sole double arylated product, 1,4-bis(3-methylpyridin-2-yl)-2,5-diphenylbenzene, in excellent yield. The regiospecific double arylation was successfully applied to the synthesis of π-conjugated polymers using aryl dibromides. The bathochromic shift of the UV-vis absorption with respect to that of the model compound, 1,4-bis(3-methylpyridin-2-yl)-2,5-diphenylbenzene, indicated the extension of the π-conjugation. The polymers exhibit photoluminescence in solutions but not in the solid state, while the corresponding model compound proved to serve as a new luminogen for the aggregation-induced emission.

In **Chapter 4**, the polycondensation of a C-H monomer possessing *N*-(8-aminoquinolyl) unit as a bidentate directing group and aryl dihalides through the C-H functionalization process and the synthesis of wholly aromatic polymers based on this

synthetic method is described. In **Section 1**, the polycondensation of *N*-(8-aminoquinolyl)benzamide and aryl dihalides via the Ru-catalyzed C-H functionalization was carried out to produce wholly aromatic polymers in high yields. Various wholly aromatic polymers were obtained from various aryl dihalides based on this polycondensation.

In **Section 2**, the three-component polycondensation of aroyl chlorides, 8-aminoquinoline, and aryl dihalides via the Pd-catalyzed C-H functionalization produced wholly aromatic polymers in moderate yields. Since the present system can be carried out by the use of simple monomers including aroyl chlorides and aryl diiodides, a variety of wholly aromatic polymers would be designed without complicated synthetic steps of the monomers.

In **Chapter 5**, the studies described in this thesis were summarized and future perspectives are described.