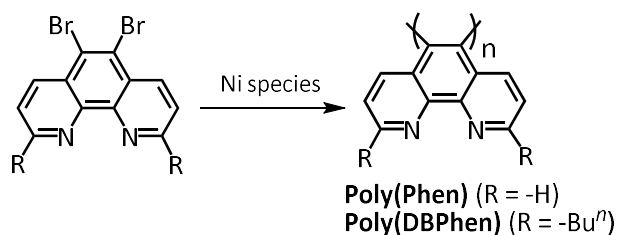




ポリ(1,10-フェナントロリン): 合成、構造およびらせん状
高分子配位子としての応用
**Poly(1,10-phenanthroline-5,6-diyl): Synthesis, Structure and
Application as Helical Polymer Ligand**

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Helical polymers are an important class of materials that find a wide range of applications in fields such as chiral recognition, nonlinear optics, and chiral catalysis. We have recently reported the synthesis, chemical structure and conformation of helical poly(1,10-phenanthroline-5,6-diyl) (poly(Phen)) and poly(2,9-di-*n*-butyl-1,10-phenanthroline-5,6-diyl) (poly(DBPhen)) as novel polymers whose main chain consists of 1,10-phenanthroline-5,6-diyl units through polymerizations via Yamamoto coupling polymerization using Ni species (Scheme 1); these polymers were designed as macromolecular ligands.¹ For poly(DBPhen), a preferred-handed conformation was constructed by helix-sense-selective polymerization using a chiral ligand.



Scheme 1. Synthesis of poly(Phen) and poly(DBPhen).¹

In this work, we studied more detailed aspects of the polymerization of 5,6-dibromo-1,10-phenanthroline leading to poly(Phen) and application of the polymer for catalytic reactions. First, Kumada-Tamao coupling reaction with Ni(acac)₂ as catalyst was introduced as a method of polymerization leading to poly(Phen). However, monomer conversions in Kumada-Tamao coupling were lower than those in Yamamoto coupling polymerization, and molar masses of the products were also lower than those of the products in Yamamoto coupling polymerization. These results may mean that coordination of 5,6-dibromo-1,10-phenanthroline and the growing chain to the Ni(acac)₂ or Mg retards polymerization reaction.

In addition, asymmetric polymerization (helix-sense-selective polymerization, asymmetric helix-chirogenic polymerization) of 5,6-dibromo-1,10-phenanthroline via Yamamoto coupling was examined using chiral ligands including (*R*)- and (*S*)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP). The polymers obtained with (*R*)- and (*S*)-BINAP's exhibited clear and intense circular dichroism (CD) spectra having mirror-image spectral shapes to each other. Because poly(Phen) has no centers of symmetry, the spectral characters strongly suggest that the polymers possess preferred-handed helical conformation.

Further, Pd-catalyzed reactions were carried out using helical, racemic and optically active poly(Phen) as ligands where the structural characters of the polymer affected activity and selectivity of catalytic reactions.

<参考文献>

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