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学位論文要約

学位論文題目　Studies on π-Stacked Helical Polyurethane and Related Small Molecules
（π-スタック型らせん状ポリウレタンおよび関連低分子化合物の研究）

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Specific conformations of chains are often seen in biological macromolecules. Among such conformations, one of the most abundant structures is helix. Helix is believed to be deeply connected to the complicated but controlled functions of living systems. Apart from biological systems, synthetic efforts have been made to a significant volume and depth to create artificial helical polymers. Helical polymerscan be categorized into the following three classes on the basis of their conformational dynamics and the presence/absence of a random conformation mediating right- and left-handed helices; (i) dynamic helix, (ii) foldamer, and (iii) static helix. As a newer conformational motif of polymer chain, π-stacked structure has been found. This structure is found in DNAs and synthetic polymers where π-electronic groups are accumulated on top of each other. Such structure is known to facilitate charge transport through a polymer chain.

Optically active, preferred-handed helical polymers can be prepared by the polymerization of asymmetric helix-chirogenic polymerization. Through this method, a preferred- or single-handed helix is produce by the influence of chirality source typically in monomer or in ligand. An often used optically active compound as a chiral monomer or monomer precursor is (R)-2,2'-binaphthy-1,1-diol ((R)-BINOL). This thesis focuses on the synthesis and structures of chiral polyurethanes using an axially chiral BINOL and a diisocyanate.

Chapter 1 overviews the backgrounds of helical polymers and π-stacked polymers. Helical polymer's structural features and synthetic methods were systematically described. Further, π-stacked conformation has been identified for DNAs and poly(dibenzofulvene) and its derivatives. Both DNAs and poly(dibenzofulvene)s are known to have a high charge mobility on the basis of the structural characteristics.

Chapter 2 discusses the addition polymerization of (R)-BINOL to 1,4-phenylene diisocyanate (PDI) togive the BINOL-based chiral polyurethane (Poly-1) and the cyclic oligomers. Poly-1 had already been made and its properties have been reported by a Chinese group, and the polymerization mechanism had been assessed and cyclic oligomers had been for the first time synthesized by Dr. T. Sakamoto and coworkers.

With these facts as a background, in this work, the author re-synthesized the polymer and related small molecules, re-confirmed their formation and structure, investigated into further details of reaction mechanisms, and proposed a conformation gathering up new and existing entries of information about the reaction and structures of the compounds. The author for the first time found that, in the early stages of polymerization, a linear dimer was generated, which can be taken as an embryonic species of the polymerization. In addition, he found an optimal condition to produce poly-1 at a high yield where the formation of small molecules was suppressed. Chain conformation is discussed on the basis of CD, UV and NMR spectra. The UV and NMR spectra confirmed that the polymer has a π-stacked structure. In addition, with the aid of MD simulations results, a 2/1 helical, π-stacked structure is proposed, which may explain the properties of the polymer already reported.

Chapter 3 is the general conclusion. Because π-stacked conformation is known to facilitate charge mobility and photo electronic properties, the polymer prepared in this work may find novel applications for which polyurethanes have never been used. The present results may provide the new insights in the fields of not only helical polymer synthesis but also high performance materials possessing chiral functions.