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## 論文審査の要旨及び審査員

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論文審査の要旨 (2000 字程度)

This thesis entitled “Chemical Modifications of Group 14-16 Element-containing  $\pi$ -Conjugated Polymers” has dealt with new synthetic approaches to produce  $\pi$ -conjugated polymers containing group 14-16 heavier elements by facile chemical modifications of  $\pi$ -conjugated polymers containing heteroles such as tellurophene, phosphole, and stannole. Unique features of the resulting  $\pi$ -conjugated polymers are also described.

In *Chapter 1* “General Introduction”, the research backgrounds related to  $\pi$ -conjugated materials, element-block-containing materials, main-chain reactive polymers, and chemical modifications of heteroatom-containing  $\pi$ -conjugated polymers are described.

In *Chapter 2* “Te-Li Exchange Reaction of Tellurophene-containing  $\pi$ -Conjugated Polymer as Potential Synthetic Tool for Diene-containing Functional  $\pi$ -Conjugated Polymers”, based on the facts that tellurophene-containing  $\pi$ -conjugated polymers are obtainable from organotitanium polymers and that the tellurium atoms in the tellurophene derivatives can be transformed into lithium atoms, the synthesis of reactive lithiated polymer precursor and its transformations into some functionalized  $\pi$ -conjugated polymers are described. The lithiated polymer thus prepared was subjected to the reactions with electrophiles such as tri-*n*-butyltin chloride to demonstrate its high reactivity.

In *Chapter 3* “Synthesis of Group 14 Element-containing  $\pi$ -Conjugated Polymers *via* Te-Li Exchange of Tellurophene-containing Polymer”, the reactions of lithiated polymer precursor to produce  $\pi$ -conjugated polymers containing heteroles of the group 14 elements are described.

In *Section 1* “Synthesis of Silole-containing Polymers *via* Te-Li Exchange of Tellurophene-containing Polymer”, the synthesis of silole-containing  $\pi$ -conjugated polymers is described. The lithiated polymer was subjected to the reactions with dimethylsilyl dichloride and diphenylsilyl dichloride to produce dimethylsilole- and diphenylsilole-containing  $\pi$ -conjugated polymers, respectively. The low-lying LUMO energy levels and interesting optical properties of the silole-containing polymers are also described.

In *Section 2* “Synthesis of Germole-containing  $\pi$ -Conjugated Polymer *via* Te-Li Exchange of Tellurophene-containing Polymer”, the synthesis of a germole-containing  $\pi$ -conjugated polymer is described. The lithiated polymer was subjected to the reaction with dimethylgermyl dichloride to produce a

dimethylgermole-containing  $\pi$ -conjugated polymer. The low-lying LUMO energy level and unique optical properties of the germole-containing polymer are also described. In addition, the presence of chemical interaction of the polymer with fluoride was demonstrated by the changes observed in the UV-vis absorption spectra.

In *Chapter 4* “Synthesis of Tellurophene-containing Polymers by Transition Metal-catalyzed Polycondensation and Their Applications as Synthetic Precursors of Heteroatom-containing  $\pi$ -Conjugated Polymers”, a  $\pi$ -conjugated tellurophene-containing polymer was prepared by the Sonogashira-Hagihara cross-coupling polymerization of 1,4-bis(2-ethylhexyloxy)-2,5-diethynyl-benzene and 2,5-di(4-bromophenyl)tellurophene, and was subjected to the reaction with *n*-butyllithium followed by dimethylgermyl dichloride to produce a dimethylgermole-containing  $\pi$ -conjugated polymer.

In *Chapter 5* “Synthesis and Applications of  $\pi$ -Conjugated Phosphole-containing Grafted Copolymers by Anionic Polymerization from Phospholyl Anion-containing Polymers”, the synthesis of phosphole-containing  $\pi$ -conjugated polymers having grafted chains by the anionic graft copolymerization of (meth)acrylates initiated from the phospholyl anion-containing polymer intermediate is described. As a consequence, the PMMA-grafted phosphole-containing polymer could be obtained which exhibits the orange fluorescence both in bulk and in solutions. The fluorescence quantum yields are comparable both in bulk and in solutions presumably due to the restrictions of the intermolecular  $\pi$ - $\pi$  interactions by the grafted PMMA chains.

In *Chapter 6* “Synthesis of Heteroatom-containing  $\pi$ -Conjugated Polymer *via* Transformation of Stannole-containing Polymer”, a 1,1-dimethylstannole-2,5-diyl-containing polymer, which was obtained from an organotitanium polymer with dimethylstannyl dichloride, was subjected to the reaction with tellurium tetrachloride followed by the treatment with aqueous sodium thiosulfate to give a tellurophene-2,5-diyl-containing polymer. The high transformation efficiency could be supported by the  $^1\text{H}$  NMR and UV-vis absorption spectra.

In *Chapter 7* “Summary”, the works presented in this thesis are summarized and future perspectives related to the present studies are described.

That is to say, this thesis has dealt with new approaches to produce  $\pi$ -conjugated polymers containing group 14-16 heavier elements by facile chemical modifications of  $\pi$ -conjugated polymers, that attained great contributions to the field of polymer synthesis. The works presented in this thesis would become of importance also in the field of the chemical industry in the near future. Therefore, this thesis is worth for doctor of engineering.

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