

ポリチオフェン誘導体を用いた 共役高分子の 電荷移動機構に関する研究

蒋 晓青

広島大学大学院生物圏科学研究科

A study on conduction mechanisms of π -conjugated polymers based on the use of chemically modified polythiophenes

Xiaoqing JIANG

*Graduate School of Biosphere Science, Hiroshima University,
Higashi-Hiroshima 739-8521, Japan*

要 旨

Conducting π -conjugated polymers have attracted considerable attention owing to their interesting molecular properties as well as their promise for providing new materials for modern technology such as organic light emitting diodes (OLEDs), field effect transistors (FETs), optical converters, molecular switches or superconductors. Polythiophene and its derivatives are the first examples of conducting polymers that are fairly stable toward oxygen and moisture both in their undoped and doped states. As a matter of fact, in addition to their stability, electroactivity and conductivity, polythiophene and its derivatives represent an almost unique class of materials in which structural versatility is associated with the conduction properties. This particularity makes polythiophene and its derivatives the most useful materials for clarification of conduction mechanisms, which is of great importance in applications such as OLED and FET. In this work, conduction mechanisms of π -conjugated polymers are investigated using chemically modified polythiophenes. We will place our attention on the following topics: 1) the contribution of interchain and intrachain charge transport to the macroscopic (bulk) conductivity, 2) the role of π -dimers, 3) the influences of π -conjugation length and 4) structure of crystalline domains in polymer films on mobility of charge carrier and 5) the nature of charge carriers in conducting polymers at various doping states. The related topics are discussed on the bases of the mobility measurements at various oxidation stages, assisted with in-situ ESR, in-situ UV-vis-NIR and cyclic voltammetric measurements.

This thesis consists of seven chapters. Chapter 1 introduces the present state of studies on conducting polymers and several techniques for measuring the charge carrier mobility including the recently developed electrochemical technique in our laboratory. In addition, properties of polythiophene and its derivatives are reviewed.

Chapters 2 to 4 are devoted to topics 1 to 3. In Chapter 2, mobilities of charge carriers in films of a copolymer consisting of a repeat unit of sexithienylene and ethylene (PSE) are measured in a wide range of

doping level. In this polymer film a possible charge transport is limited to an interchain path. The mobility in the low doping regime, corresponding to that of polarons, is evaluated as $10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, comparable with polaron mobilities in polythiophene films where hopping transports via interchain and intrachain routes are both feasible. The coincidence suggests strongly a potential role of the interchain hopping transport in the conduction mechanisms of common conducting polymers. As the doping level increases, the mobility once falls down to $0.4 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and rises up to $6 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Based on spectroelectrochemical and ESR measurements of the PSE film, the decrease of the mobility is interpreted in terms of the generation of cation radical π -dimers that are inactive in charge transport. The mobility increase in a high doping region is ascribed to some structural change of the polymer network, leading to enhancement of the interchain hopping probability.

In Chapter 3, chemical and electrochemical oxidations of a series of copolymers consisting of a repeat unit of monosilanylene and oligothiopylene (PS_nT , $n=5-9$, where n denotes the ring number of an oligothiopylene unit) are studied. It is found that the oligothiopylene unit of each copolymer is oxidized in the first oxidation step to form cation radicals in equilibrium with π -dimers, and in the subsequent oxidation step to yield dication. Energies of all absorption bands for these oxidized species and oxidation peak potentials for PS_nT in solution increase linearly with the increase of the reciprocal of the size of the oligothiopylene unit. The formation of π -dimers is found to be favored by extending the oligothiopylene unit of PS_nT . The equilibrium constant for the formation of π -dimers for PS_5T is evaluated as $5 \times 10^4 \text{ M}^{-1}$. Reversible generation of π -dimers observed with all polymers enables us to perform further studies for clarifying the role of π -dimers in the conduction mechanisms of conducting polymers.

In Chapter 4, mobilities of charge carriers in thin films of PS_nT s are measured as a function of doping level in order to elucidate the influence of π -conjugation length on the mobility. Mobilities of charge carriers in these polymer films, where intrachain hopping transport is prohibited, are constant in the low doping regions below 1%: $0.8 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for PS_5T and $3 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for PS_6T to PS_9T . As the doping level increases mobilities begin to increase for all films. The onset of mobility increase starts at relatively lower doping levels for polymers with longer π -conjugation lengths. The mobility enhancement follows also the increase of the π -conjugation length, although 30 times enhancement of mobility for PS_9T is still smaller than the four order-of-magnitude increase of mobility observed earlier with poly(3-methylthiophene). The results are discussed electrochemically and spectroelectrochemically from a viewpoint of involvement of polarons, π -dimers, and bipolarons as possible charge carriers in the conduction mechanisms.

Chapters 5 and 6 are devoted to the systematic study on the influences of stacking structures in polymer films on the transport properties of conducting polymers. Recently, FET studies have shown that the mobility of charge carriers in a poly(alkylthiophene) (PAT) film is greatly influenced by the structure and orientation of polymer chain in the crystalline domains, which can be controlled by the regioregularity of the sample. However, these mobility studies are restricted to those for neutral or undoped films because of limitations of the FET technique. Little information is available so far on mobilities in PAT films at various oxidation stages. In Chapter 5, mobilities of positive charge carriers in poly(3-hexylthiophene) (PHT) films of 54%, 70%, 81%, and 97% in regioregularity are electrochemically measured over a range of doping levels. Irrespective of the difference in regioregularity, the increase of doping level leads to a decrease of mobility for all the PHT films, followed by a drastic increase at ca. 1% doping level. As the sample regioregularity is increased, the mobility vs. doping level plot shifts upward parallel to the ordinate. The results show that better ordered stacking structures enhance mobilities, but affect little features of the mobility change by doping. The common doping level of ca. 1% for

the onset of the drastic mobility increase implies that the π - π stacking structures facilitating a charge transport in neutral or lightly doped PHT films are not responsible for the evolution of metallic conduction in PHT films.

In Chapter 6, the electrochemical, optical, ESR and conducting behaviors of the regioregular and regiorandom PHT films are investigated in detail. The natures of charge carriers at various doping states are discussed on the bases of in-situ optical and ESR measurements. The high mobility in a regioregular PHT film in the low doping region is ascribed to the generation of two-dimensionally delocalized polarons in the self-ordered stacking lamellae structure. The initial decrease in the low doping regime is ascribed to the microstructure change of the films caused by doping. The remarkable mobility increase is found to relate to the evolution of metallic conduction.

Chapter 7 summarizes the results obtained throughout this study.

References

1. **X. Jiang**, Y. Harima, Lihua Zhu, Y. Kunugi, K. Yamashita, M. Sakamoto, M. Sato, Mobilities of charge carriers hopping between π -conjugated polymer chains, *Journal of Materials Chemistry*, **11**, 3043-3048 (2001).
2. **X. Jiang**, Y. Harima, K. Yamashita, Y. Tada, J. Ohshita, A. Kunai, Doping induced change of carrier mobilities in poly(3-hexylthiophene) films with different stacking structures, *Chem. Phys. Lett.*, **364**, 616-620 (2002).
3. **X. Jiang**, Y. Harima, K. Yamashita, Y. Tada, J. Ohshita, A. Kunai, A transport study of poly(3-hexylthiophene) films with different regioregularities. *Synth. Met.*, **135-136**, 351-352.
4. **X. Jiang**, Y. Harima, K. Yamashita, A. Naka, M. Ishikawa, Optical and electrochemical properties of a series of oligothiophylene-monosilanylene copolymers in solution, *Journal of Materials Chemistry*, **13**, 785-794 (2003).
5. Y. Harima, **X. Jiang**, Y. Kunugi, K. Yamashita, A. Naka, M. Ishikawa, Influence of π -conjugation length on mobilities of charge carriers in conducting polymers, *Journal of Materials Chemistry*, **13**, 1298-1305 (2003)