

σ - π 共役系を持つオリゴチエニレン-オリゴシリニレン
コポリマーの電気化学的及び光学的研究*

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Electrochemical and Optical Studies on σ - π -Conjugated
Oligothienylene-Oligosilanylene Copolymers

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要 旨

Conventional conductive polymers such as polythiophene and polyaniline have extensively conjugated π -electron systems in the polymer chain. Through appropriate chemical or electrochemical oxidation or reduction, they can be converted from insulators into semiconductors or conductors. Because of their unique physical/chemical properties and various promising applications, the conductive polymers take an important position in the development of novel functionality materials and have become a subject of considerable interest for both academic and industrial researchers in different fields such as solid-state physics, chemistry, and electrochemistry. Oligothienylene-oligosilanylene copolymers studied in this thesis are a new type of conductive polymers. They consist of alternating π - and σ -conjugated units in a polymer chain, being hence referred to as σ - π -conjugated polymers, and are soluble in common organic solvents. They are recently found to have potential applications as materials in photoresists, conductive substrates, are electro-luminescent layer in large-area light-emitting devices. This work is motivated primarily by our interest from a practical viewpoint of the possible applications of these materials to photoresists, optoelectronic devices and so on. However, little is known about the electrochemical properties of the σ - π -conjugated polymers, and the optical properties of some copolymers are also scatteredly reported in the literature. Studies of their electrochemical and optical properties will provide essential information for promoting performances in practical devices. The stability of these copolymers is also a subject of great importance from a practical point of view. Moreover, an understanding of the influence of

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the σ - π -interaction on the properties of the σ - π -conjugated copolymers is of great interest from an academic point of view. Hence, it is attempted to understand their electrochemical redox process, to clarify the influences of oligosilanylene on the electrochemical properties of the copolymers, and to characterize the species generated in the copolymer during the electrochemical oxidation, being very essential to clarification of the conduction mechanism for a conductive polymer. The present work aims further at the optical properties of the σ - π -conjugated copolymers, which will lead to a better understanding of the σ - π -interaction. To our best knowledge, the present work is the first systematic study on electrochemical and optical properties of the oligothiénylene-oligosilanyene copolymers.

This dissertation consists of nine chapters. In Chapter 1, the present state of studies of polythiophenes, polysilane and σ - π -conjugated thiophene-silane copolymers is reviewed. Chapter 2 gives a brief description of the synthesis of thiophene-silane copolymers used in the present work. These copolymers have a general chemical structure shown in Fig.1, and consist of alternating π - and σ -conjugated units in a polymer chain. The numbers of silicon atoms (m) and thiophene rings (n) in the repeat unit of these copolymers are adjustable as $m=1\sim 3$ and $n=1\sim 5$, respectively. For convenience, the names of these copolymers are abbreviated correspondingly as $MSnT(m=1)$, $DSnT(m=2)$ and $TSnT(m=3)$.

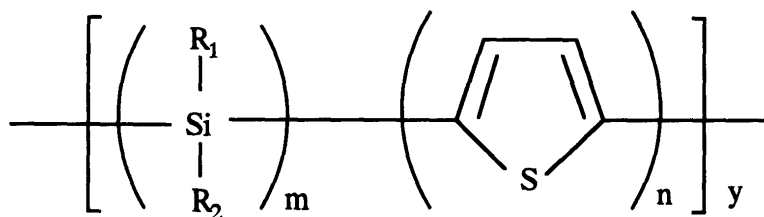


Fig. 1 Chemical structures of the copolymers $mSnT(n=2-5, \text{ except } n=1 \text{ for } DS1T)$.

$TSnT$: $m=3, R_1=R_2=CH_3$; $DSnT$: $m=2, R_1=R_2=C_2H_5$; $MSnT$: $m=1, R_1=R_2=C_2H_5$;

$MSnT-OEt$: $m=1, R_1=C_3H_7, R_2=C_2H_5O$.

In Chapters 3 to 7, the electrochemical properties of thin films of these copolymers are investigated in Et_4NBF_4 /acetonitrile (MeCN) solutions using cyclic voltammetry, potentiostatic oxidation, electrochemical quartz crystal microbalance (EQCM) and spectroelectrochemical measurements. Chapter 3 is devoted to the $DSnT$ series. The polymer films have been found to show two pairs of main redox peaks in the cyclic voltammograms, which is similar to the redox behavior of capped oligothiophenes in solution. However, we studied the spectroelectrochemistry of their films by limiting the upper potential limit at value less positive than the second oxidation peak, because the polymer is very unstable at potential of the second oxidation peak. In multicyclic voltammograms of the DS

5T film in MeCN, there are an oxidation peak and a reduction peak superimposed on a cathodic plateau, which are due to switching reactions of doping/dedoping. The shape of the multicycle voltammogram depends little on the scan rate of potential, but the first voltammogram changes substantially in shape as the scan rate decreases. By decreasing scan rate, the oxidation peak in the first voltammogram split into two and then three peaks. Such a splitting of the first main oxidation peak occurs also for the DS3T and DS4T films. Spectroelectrochemical analysis suggests that these oxidation peaks be ascribed to decomposition (peak A) and doping (peak B and C) processes of the polymer. Characterization of the produced decomposition products of the DS n T films indicates clearly that the electrochemical decomposition of the polymers originates from an electrochemical cleavage of Si-Si bonds. The degradation of the polymer films is slow, and no complete dissolution of the film is observed mainly due to re-deposition of some solid substance onto the film resulting from the further oxidation of generated product. Therefore, the electrochemical anion doping of the polymer films is feasible.

In Chapter 4, electrochemical oxidation of thin films of the TS n T is studied. Because of the electrochemical cleavage of the Si-Si-Si bonds, the TS n T copolymers are found to be electrochemically less stable than the DS n T copolymers. Except for this point, the TS n T copolymers show electrochemical properties similar to those of the DS n T. By EQCM measurement, it is found that there are two types of Si-Si cleavage, i.e., a directly electrochemical degradation at a lower potential and an electrochemical-chemical cleavage related to the doping of the copolymer film at higher potentials.

In Chapter 5, the electrochemical oxidation of films of the copolymers using TS5T as a representative is further investigated in electrolyte solutions containing other anions such as PF_6^- , ClO_4^- , F^- and NO_3^- . The experimental results indicate that the electrochemical-chemical Si-Si cleavage induced by doping is dependent on the anions present in electrolyte solution. It is found from fluorescence, EQCM and FT-IR measurements that Si-Si-Si bonding is weakened by electrochemical doping in the π -conjugated segment, resulting in promotion of the bonding in MeCN solutions containing BF_4^- and PF_6^- anions, whereas such a doping-enhanced cleavage of the Si-Si-Si bonding is relatively negligible in ClO_4^- solution. This difference is possibly related to some specific interaction between the Si atoms in the polymer chain and the F atoms in the dopant. In F^- solution, on the other hand, the polymer film undergoes electrochemical fluorination and/or chemical dissolution. The electrochemical oxidation of the polymer film in NO_3^- solution leads to nitration of the polymer film. Based on the results in Chapters 3~5, possible mechanism is proposed for electrochemical oxidation of the σ - π -conjugated copolymers in electrolyte solutions containing BF_4^- , PF_6^- and ClO_4^- anions, and is shown in Fig.2.

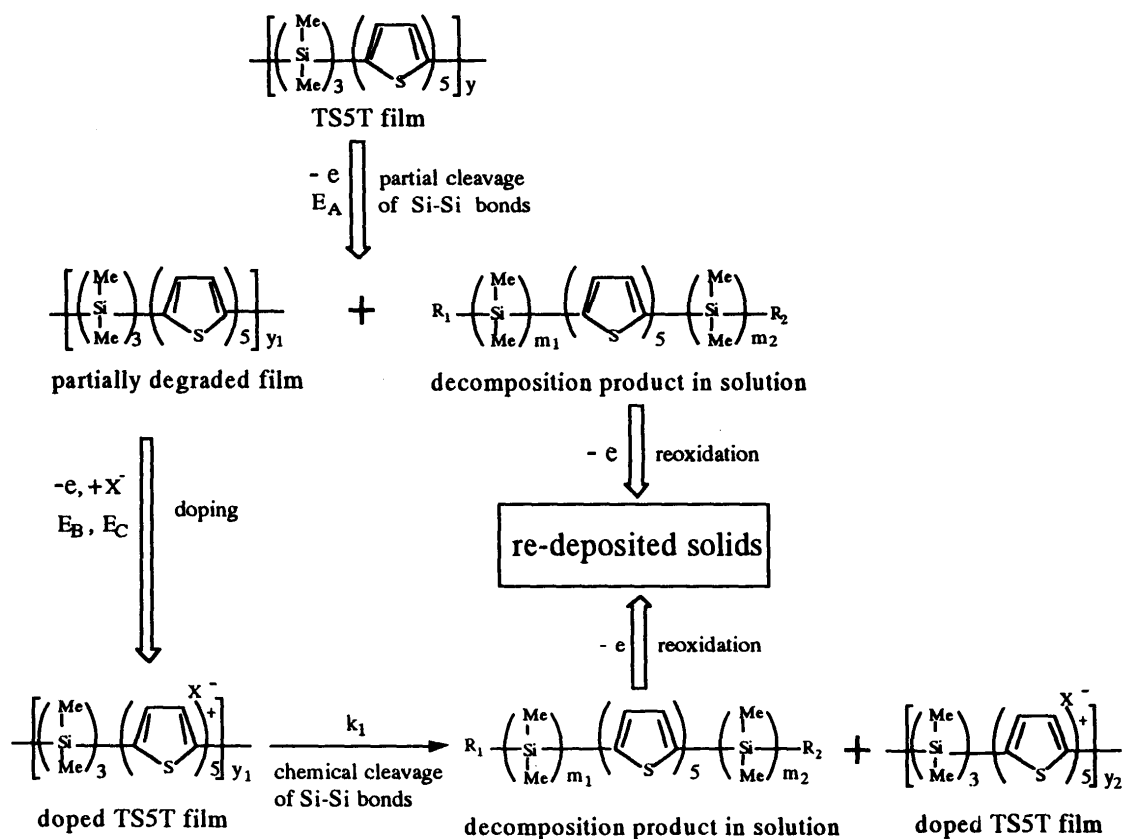


Fig.2 A mechanism for electrochemical oxidation of a TS5T film in MeCN solutions containing X^- anions, where $X^- = \text{BF}_4^-, \text{PF}_6^-, \text{or } \text{ClO}_4^-$; $m_1, m_2 = 1 \text{ or } 2$; $y > y_1 > y_2$. E gives potentials of related oxidation peaks in cyclic voltammograms, and k_1 is a rate constant.

Chapter 6 reports the influences of block sizes (m and n), namely, numbers of silicon atoms (m) and thiophene rings (n) in the repeat unit of these copolymers, on electrochemical properties of the MS_nT , DS_nT and TS_nT series copolymers. The MS_nT polymers ($m=1$) are found to be relatively stable. In the cyclic voltammograms, two pairs of redox peaks occur generally, though the second oxidation peak is hardly seen for MS_2T and MS_3T due to the instability of the radical cations generated in their main chains. In-situ measurements of the absorption spectra of the MS_5T film at different potentials support that the oxidation leads to doping of the polymer film. It is found that the redox behaviors of the polymers are mainly dependent on the oligothiophylene block size (n) and the oxidation peaks shift significantly to a cathodic direction as n increases. The DS_nT and TS_nT films are possibly decomposed and dissolved partially by electrochemical oxidation because of the Si-Si cleavage. Voltammetric behaviors of the DS_nT and TS_nT films are correspondingly similar

to those of the MS n T films, but affected by the Si-Si cleavage process. An oxidation subpeak due to this cleavage reaction occurs in the voltammograms of these films obtained at slow scan rates. The onset potential of this cleavage reaction or the dissolution of the film decreases as the oligosilanylene block size (m) increases. In the voltammograms at faster scan rates, the doping process dominated over the possible Si-Si cleavage reaction. This permits a comparison between the potentials of the oxidation peaks of these copolymer films.

If it is found that for a given n , the oxidation peak shifts cathodically as m increases, especially for smaller values of n . This is possibly related to the effects of the σ - π -conjugation.

In electrochemical oxidation, the films of the copolymers containing Si-Si bonds more or less suffer from decomposition and dissolution due to partial cleavage of Si-Si bonds. This kind of decomposition of the polymer films becomes more difficult as the oligosilanylene block size decreases, and not observed for the copolymers containing no Si-Si bond ($m=1$). Along with the possible cleavage of Si-Si bonds, the copolymer films are able to be anion doped by electrochemical oxidation, via a two-step oxidative doping process. The potentials of the oxidative doping peaks are found to show a cathodic shift as the oligosilanylene block size increases because of the effects of the σ - π -interaction in the repeat units of the polymer chains. This kind of interaction is favorable to the stabilization of the cations and dications generated in the polymer chain.

In Chapter 7, electrochemical doping and in-situ UV-vis-NIR spectroelectrochemical properties of thin films of some copolymers with $m=1$ are investigated in MeCN, together with their chemical doping conducted in dichloroethane. The films of MS5T, MS5T-OEt and MS4T-OEt exhibit a two-step one-electron oxidation process due to the oxidation of the oligothiénylene unit in these copolymers. In the first oxidation step stable cation radicals and π -dimers are generated in these copolymer films, resulting in a doping level of about 0.2 for MS5T and MS5T-OEt, or of ca. 0.25 for MS4T-OEt. In the second step dications are formed, accompanied by degradation of the polymers to a greater or lesser extent. As the doping level is increased by increasing the oxidation potential, the consecutive formation of the cation radicals, the π -dimers and the dications is clearly observed in the in-situ UV-vis-NIR absorption spectra of the polymer film. Fitting the integrated absorption intensities of the individual absorption bands gives the equilibrium constant for the dimerization of the cation radicals in the MS5T-OEt film as $K=10 \text{ M}^{-1}$.

Meanwhile the bipolaron and the possible π -dimer generated in a conductive polymer film are indistinguishable from each other in spectroscopic and ESR measurements. It is hard to investigate their relative contributions to the conduction in a conductive polymer. We have found that at potentials below ca. 0.75 V, the MS5T-OEt film is stable and, only the cation radicals and their π -dimers are produced in the film. Therefore, this polymer is a proper one for studying the role of the π -dimer in the conduction mechanism of conductive polymers. Study on the contributions of the radical cations and their π -dimers to the conduction process in the MS5T-OEt film is undergoing in our laboratory.

In Chapter 8, We have studied photophysical properties of three series of σ - π -conjugated polymers containing alternatively oligosilanylene and oligothiénylene blocks in dioxane

solution. Because of the insertion of intrinsically non-conjugated oligosilanylene units into the polymer chain, the chromophore in the σ - π -conjugated copolymers is apparently composed of the oligothiophene block. That is, the polymers have spectroscopic features similar to their analogous oligothiophenes correspondingly. As the oligothiophene block size in the polymers increases, both the absorption and fluorescence bands shift to long wavelengths, and their energies decrease for $n=2-5$. The chemically tunable fluorescence of the polymers by a proper choice of the oligothiophene block size seems very interesting for their applications as luminescent materials in LEDs. The σ - π -interaction in the polymers becomes more important with decreasing the size of the oligothiophene block. The σ - π interaction through C-S-C single bond route in the thiophene block in the polymer chain may reduce the intersystem crossing rate in the decay of the singlet excited state of the conjugated polymers, therefore considerably higher fluorescence quantum yields and fluorescence lifetimes are observed for the copolymers having thiophene or bithiophene blocks. In consideration of the relative importance of the σ - π interaction, it is necessary to divide the σ - π -conjugated polymers into at least two groups for studying systematic effects of the block size m and of the substitution at the oligothiophene and/or oligosilanylene blocks on photophysical properties of the polymers: One group include the polymers having smaller oligothiophene block size ($n=1,2$), and another one having larger oligothiophene block size ($n=3-5$). The σ - π interaction show stronger effect on photophysical properties of the polymers for polymers of smaller oligothiophene block size ($n=1$ or 2) than for the polymers of larger oligothiophene block size ($n \geq 3$). Optical properties of the copolymers are investigated in dioxane solution.

The last chapter, Chapter 9, summarizes the most important results obtained in Chapters 3 through 8. (1) The copolymers consisting of oligothiophene units bridged by monosilyl units are electrochemically stable, whereas the copolymers containing Si-Si bonds show fairly poor stability due to the electrochemical cleavage of the Si-Si bonds. (2) The copolymers are able to be electrochemically anion doped via a two-step oxidative doping process. (3) The doping of the copolymer films results in electrochromic change. As the doping level of the copolymer increases, radical cations, π -dimers of radical cations, and then dications are produced successively. One of the copolymers, MS5T-OEt, is found to be suitable for being used to study the role of the π -dimeration in the conductive mechanism of conjugated polymers, which is undergoing in our laboratory. (4) The fluorescence wavelength of the copolymers can be controlled by adjusting the size of the oligothiophene blocks. This is interesting from view point of applications in electroluminescence devices. (5) The optical and electrochemical properties of the copolymers are strongly dependent on the σ - π -interaction in the copolymers.

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