A possibility for generation of two species of charge carriers along main-chain and side-chains for a $\pi$-conjugated polymer

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Abstract. Iodide doping produces charge carriers in $\pi$-conjugated polymers. Solitons can be generated in the case of polyacetylene, and polarons in the case of aromatic-type conjugated polymers. We synthesized a conjugated main-chain/side-chain polymer, which consists of polyene in the main-chain and aromatic-type conjugated units in the side-chains. Based on the SSH (Su, Schrieffer, Heeger) theoretical model of solitons in one-dimensional conjugated polymers, we experimentally carried out chemical doping to the main-chain/side-chains conjugated polymer. Generation of the charge carriers was examined by electron spin resonance spectroscopy. This study may lead to realization of a dual doping system of solitons and polarons in $\pi$-conjugation expanded to two-dimensional directions in polymers.

1. Introduction
$\pi$-Conjugated polymers consist of alternation of single and double bonds. The main-chains have delocalised $\pi$-electrons. Polyacetylene is a typical conjugated polymer. It shows metallic refraction because of its highly developed conjugated system, and displays quite high electrical conductivity comparable to metals such as copper, after vapor phase doping by iodine (chemical doping), accompanied by insulator-metal transition [1]. In this case, the charge species of polyacetylene can be characterized as solitons [2].

Aromatic type conjugated polymers also show conductivity upon chemical doping. In the case of aromatic type conjugated polymers, the charge carriers are referred to as polarons and bipolarons [3–4].

In the present study, we synthesize a $\pi$-conjugated polymer having a conjugated system in both the main-chain and the side-chains. The side-chains are directed perpendicular to the main-chain. After the doping by iodine, charge carriers are generated in both side-chains and main-chain, producing solitons in the main-chain and polarons or bipolarons in the side-chains. This can be referred to as a double doping process in conjugated polymers.

We have prepared a polyacetylene derivative with aromatic-type side-chains and doping effect for the polymer. Then, we experimentally consider charge carriers along the $\pi$-conjugated system.

The SSH model in a one-dimensional system was proposed for solitons of polyacetylene [2]. A ground state of polyacetylene described by the model as follows,

$$H_{SSH} = H_{\pi} + H_{\pi-ph} + H_{ph}$$  (1)
Here, the dimerization coordinate and the lattice constant are defined by $u_n$ and $\alpha$, respectively. To clamp $u_n$ at twofold ground state $E(u_0) = E(0)$, $(-1)^n u_n$, the system supports nonlinear excitations.

\[ \varphi_n = (-1)^n u_n. \]  

So that,

\[ \varphi_n = u_0, E(u_0), \]  
\[ \varphi_n = -u_0, E(-u_0). \]

If $\varphi_n$ changes very slowly from $-u_0$ to $u_0$, there will be large range surrounding $n = 0$ where condensation energy is reduced, and it rises again. Width of the solitons is expressed by $\xi$.

\[ \varphi_n \equiv u_0 \tanh [(n - n_0)\alpha/\xi]. \]  

And if there is a solution of $E_0$, because the spectrum of $H_{cl}$ is symmetric about $E_0$, then $H_{cl}$ satisfies

\[ \sum |n| E_{cl} |m\rangle\psi_0 = 0. \]

This model has been proposed by Su, Schrieffer, and Heeger for polyacetylene [2]. In the case of aromatic conjugated polymers [3–5], chemical doping allows generation of polarons along the main-chains [6]. Figure 1 shows an example of polarons along poly($p$-phenylene).

\[ \text{Figure 1. Radical cations (polarons) of poly($p$-phenylene).} \]

2. Results and discussion

2.1 Synthesis polymer

Firstly, the disubstituted acetylene monomer was synthesized with the Sonogashira coupling reaction by using Pd(0) and CuI catalysts in the base condition. Next, the monomer was polymerized with TaCl5 catalyst in toluene solution via metathesis mechanism. The resultant polymer was washed with a large amount of methanol, the product was collected by reprecipitation followed by drying in vacuum to yield a yellow polymer with fluorescence.

2.2 Chemical doping for polyacetylene derivatives

Polyacetylene shows high electrical conductivity upon vapor phase doping by iodine as an electron accepter for generation of charge carriers.
The chemical structure of di-substituted polyacetylene is shown in Figure 2.

![Chemical structure of di-substituted polyacetylene](image)

**Figure 2.** Neutral state of polymers

Chemical vapor phase doping by iodine produces charge carriers along the main-chain as follows,

![Chemical structure showing radical cations in the main-chain](image)

**Figure 3.** Radical cations in the main-chain

In the case of the polymers having conjugated substituent located perpendicular to main-chain, the side-chains can also be doped with an electron accepter, resulting in formation of polarons in the aromatic group in the side-chains.

![Chemical structure showing radical cations in the polymer](image)

**Figure 4.** Radical cations in the polymer
Furthermore, main-chain and side-chains doping can be performed. Figure 4 shows a plausible structure of generation of charge carriers along both the main-chain and the side-chains upon iodine doping.

Electron spin resonance (ESR) of the di-substituted polymer with in-situ iodine doping was carried out. In the undoped state the polymer shows no ESR signal. The Lorenz line shape of the ESR signal appeared with iodine doping. Increase of spin concentration and line width were observed. The g-value increased slightly to 2.00393 (60 min doping) from \( g = 2.00378 \) (10 min doping) with heavy doping. Line width of the peak-to-peak (\( \Delta H_{pp} \)) increases to 0.29 mT (60 min) from 0.19 mT (10 min). A small shoulder appeared in the spectral form in the heavy doped state. Heavy doping may allow formation of solitons and polarons in both the main-chain and the side-chains, but evidence of solitons and polarons cannot be separated in the spectroscopy measurement. Furthermore, the side-chains may play a role of stabilizer for charge carriers.

Electrical conductivity upon iodine doping of the polymer increased to \( \approx 4.9 \times 10^{-5} \) S/cm (obtained with four-point probe method at room temperature) from insulator range, indicating occurrence of electrical conduction by generation of the charge carriers.

![Electron spin resonance (ESR) spectroscopy results of in-situ iodine doping of the polymer.](image)

**Figure 5.** Electron spin resonance (ESR) spectroscopy results of in-situ iodine doping of the polymer. Blue line: 0 min of doping time; green line: 10 min; red line: 60 min.

Increase of charge carrier indicates increase of radicals of polymer. In other words, the ESR results suggest generation of charge carrier in entire structure of the di-substituted polyacetylene. Increase of conductivity and existence of paramagnetic species for the polymer implies generation of solitons (radical cations along the polyene) and polarons (radical cations along the aromatic units) by iodine doping.

Temperature dependence on inverse of resistance (1/R) for the heavy-doped sample with iodine vapor was examined (Figure 6). 1/R (\( \propto \sigma \)) values of the doped polymer decreased with decrease of temperature. This is a typical behavior of semi-conducting polymers. The 1/R vs. 1/T plots for the sample clearly shows an inflection point at 258 K.

2.3 Molecular form

Computer modeling evaluated the ideal form of the polymer, indicating steric repulsion between substituents. The distortion introduces deformation of linear shape in the main-chain, resulting in
limitation of expansion of the π-conjugated system. Also, the perturbation might restrict free movement of charge carriers along the main-chain.

![Graph showing 1/R vs. 1/T](image)

**Figure 6.** Inverse of resistance (1/R) as a function of T for the heavy doped sample with iodine. Inset shows 1/R vs. 1/T plots.

However, the computer simulation demonstrated that the entire molecular shape is linear, and the main-chain (inside of substituents described by the balls in Figure 7) forms helical structure. The charge carrier on the main-chain can move along the helical architecture.

![Computer simulation of the polymer described by balls model](image)

**Figure 7.** Computer simulation of the polymer described by balls model. Geometries of this polymer have been optimized at the MMFF (Merck Molecular Force Field method, developed at Merck).

**Conclusion**
A possibility of generation of solitons along the di-substituted polyacetylene derivative is discussed. Restriction of mobility of the charge carrier along the main-chain due to deformation of linear shape of the main-chain may occur because of steric hindrance between side-chains. ESR results strongly
suggest generation of charge carriers. This can be related with double doping models for polyphenylenevinylene [7].

**Techniques**

Samples were synthesized in an inert gas with Schlenke tubes. ESR measurements of the polymer were carried out with a JEOL JES TE-200 spectrometer with 100 kHz modulations. Electrical conductivities and resistance for the sample were obtained with Mitsubishi MCP-T610 and Hioki SM8213. $1/R$ vs. $T$ plots were obtained with two-probe method.

**References**

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