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Studies on electrical transport properties of a novel n-type polymer containing tripylborane and fluorene moieties

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Abstract

An organoboron polymer, poly[(2,4,6-triisopropylphenyl)borylenevinylene-2,7-fluorenylenevinylene], has been synthesized by hydroboration polymerization with 2,4,6-triisopropylphenylborane and 2,7-diethynylfluorene. The polymer is π-electron deficient due to boron atom contained in its main-chain and the π-conjugation length in it is extended *via* the vacant *p*-orbital of the boron atom. It has been found that the polymer shows an electrical conductivity of about 10^{-6} $\mathrm{Scm^{-1}}$ by n-doping with triethylamine at RT. By continuous photo-excitation of ITO-Polymer-Au cells, it has been proved that the polymer is an n-type conductor. In addition, by pulsed photo-excitation of the cell, it has been verified that the drift mobility of electron is about five times higher than that of hole. The n-type electrical transport properties of the polymer have been also associated with an anodic wave that appears at about −1.17V in cyclic voltammograms and is ascribable to n-doping.

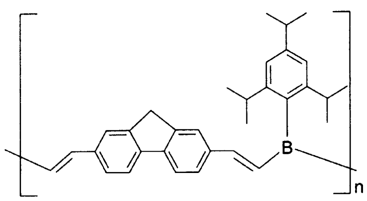
Keywords: Conjugated polymers, Conducting polymers, Transport measurements, Photoconductivity

1. Introduction

π-Conjugated polymers have attracted a great deal of attention to their potential utility especially in the field of organic electronic devices. However, for the future development in this field, it is desired to synthesize n-type π-conjugated polymers which are versatile for electron transport material and negative electrodes. This is mainly due to the reason that most of π-conjugated polymers are p-type conductors.

Recently, novel π-conjugated organoboron polymers have been synthesized by hydroboration polymerization of aromatic diynes and organoboranes, where the π-conjugation length is highly extended *via* the vacant *p*-orbital of boron atom [1]. The boron contained regularly in the polymer backbone is an electron deficient heteroatom in comparison with carbon in the same backbone. Therefore, the organoboron polymers are inherently a π-electron deficient system. This characteristic feature of π-electron deficient π-conjugation in organoboron polymers leads us to expectation that they behave as n-type conductors when carriers are injected. In our previous study of electrical conductivity based on carrier injection with a chemical doping method, we obtained a preliminary result that the organoboron polymer comprised of tripylborane and fluorene shows higher conductivity when electron is injected with a weak electron donor (triethylamine) than when hole is injected with a typical electron acceptor (I_2) at RT [2]. This result strongly suggests that the π-conjugated organoboron polymers are n-type conductors as expected. To obtain more definite evidence of n-type conductors, measurements of stationary-state current and/or transient current of photocarriers are quite valid and more direct.

For the present studies, we prepared poly[(2,4,6-triisopropylphenyl)borylenevinylene-2,7-fluorenylenevinylene] (**1**). To confirm that **1** is an n-type polymer, we have reexamined the electrical conductivity of **1** by chemical doping and then tried measurements of stationary-state photocurrent and drift mobility of carriers generated by continuous and pulsed photo-excitation of **1**, respectively. In the present report, the n-type properties of **1** are verified and also discussed in connection with cyclic voltammograms of **1**.



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2. Experimental

The π-conjugated organoboron polymer **1** used in the present studies was synthesized in THF solution by hydroboration polymerization with 2,7-diethynylfluorene and 2,4,6-triisopropylphenylborane according to the method described elsewhere [1]. The molecular weight of the polymer was as follows. M_n: 2690; M_w: 5400.

A thin cast film of the polymer with desired thickness (d ≈10μm) was prepared on the ITO-coated side of a quartz plate using a toluene solution of **1**. After drying the film under vacuum, Au was evaporated onto the polymer film to form an ITO-Polymer-Au cell, the ITO side of which is transparent. For observation of stationary-state photocurrent and drift mobility, light irradiation of 425nm wavelength on the polymer surface was always performed through the ITO-coated side of the cell with a xenon lamp of 500W and a xenon flash lamp of 20W, respectively. The polarity of bias voltage was alternately changed for each measurement of electron and hole currents, where electron currents were traced with a digital oscilloscope by setting the Au-electrode side in positive polarity.

Cyclic voltammetry was run in 0.1M THF solution of tetrabutylammonium perchlorate (*TBAP*) using a Pt-electrode *vs.* Ag/Ag$^+$-electrode. Cyclic voltammograms were usually recorded at the sweep rate of 100mVs^{-1} in the potential range between −2.0 and +1.0V.

For measurements of electrical conductivity based on carrier injection by chemical doping with triethylamine (TEA) and I_2, the previous procedures were exactly duplicated in all runs [2].

All the experiments stated here were carried at RT.

3. Results and Discussion

3.1 Electrical conductivity during chemical doping

Originally the polymer **1** is an insulator. When **1** was doped with TEA and I_2, the electrical conductivity (σ) changed along with doping time. The maximum conductivity σ_{max} achieved with TEA was about two orders higher than that with I_2 as shown in Fig.1, being similar to the preliminary result. This fact suggests again that **1** is electrically a novel class of n-type π-conjugated polymers. For the appearance of electrical conductivity by doping with TEA, we proposed a Lewis acid-base reaction model [2]. According to this model, it can be predicted that the drift mobility of electron in **1** is fairly large compared with the drift mobility of hole, and that the amount of charge donated to boron from TEA is rather small on account of the weak interaction between boron in the polymer backbone and nitrogen in TEA, as discussed in the previous paper [2]. Concerning the drift mobility of electron and hole, the actual magnitude will be given in Section *3.3*, where electron and hole were injected in the polymer by a photo-excitation method.

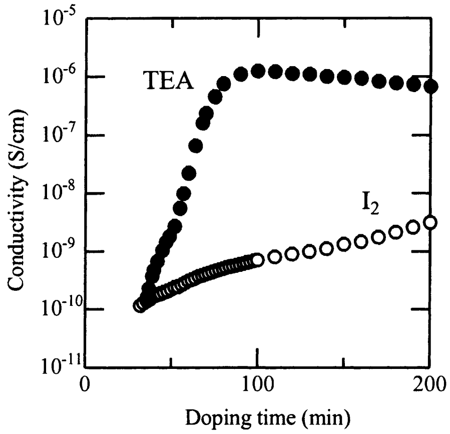

Fig.1. Electrical conductivity of **1** during chemical doping with TEA and I_2 vapor at RT.

3.2 Stationary-state photocurrents

The polymer **1** has an intense optical absorption band due to the π-π* transition of polymer backbone. The band peak locates at 414nm and its molar extinction coefficient ε is about 9,600Lcm^{-1}M^{-1}. Since the bandwidth is rather large, ε is still high at 425 nm. Therefore, when ITO-Polymer-Au cells are irradiated, the 425nm light is absorbed in a depth much shorter than the polymer thickness and produces a sheet of carriers on the polymer surface of the ITO-coated side in the cell. It is properly speculated that an equal number of positive and negative carriers is initially generated by the photo-excitation.

Before photo-excitation of the cell, the dark current density of about 10^{-13}Acm^{-2} was observed for both of electron and hole in vacuo and also in air up to the electric field strength of $2 \cdot 10^4$Vcm^{-1}. However, the dark current of electron in vacuo was slightly higher than that in air and the reverse was observed in the dark current of hole.

When the cell was irradiated continuously with 425nm

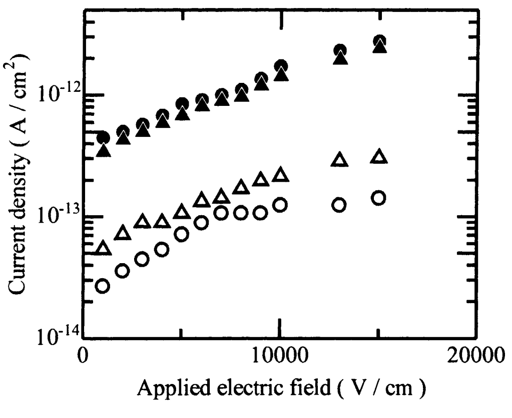

Fig.2. Photocurrent density dependent on applied electric field. ITO-Polymer-Au cell was continuously excited at RT with 425nm light from a xenon lamp of 500W. Closed circle and closed triangle: electron current in vacuo and in air. Open circle and open triangle: hole current in vacuo and in air.