

Electrical Conductivity of Poly(2-ethynylthiophene) and Poly(2-ethynylfuran) Doped with Electron Acceptors

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SYNOPSIS

The electrical conductivity of poly(2-ethynylthiophene) (P2ET) and poly(2-ethynylfuran) (P2EF) doped with electron acceptors such as iodine, bromine, and ferric chloride was investigated. The maximum electrical conductivities of P2ET and P2EF doped with iodine were $3 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$ and $5 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$, respectively. The electrical conductivity was nearly independent with increasing molecular weight. The spectral measurements such as UV-visible, infrared, electron paramagnetic resonance, thermogravimetric analysis, and X-ray diffraction were also carried out.

INTRODUCTION

There have been many studies on the preparation and electrical conductivity of charge-transfer complexes consisting of electron-donating polymers and low molecular weight electron acceptors.^{1,2} Poly(phenylacetylene),³ poly(*N*-ethynylcarbazole),⁴ poly(vinylpyridine)s,^{5,6} etc have been used as electron-donating polymers. Organic electron acceptors such as 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ), etc. and inorganic acceptors such as iodine, bromine, and Lewis acids were used to dope electron-donating polymers.

In fact, when *cis*- or *trans*polyacetylene films are doped with electron acceptors such as halogens and arsenic pentafluoride, they show metallic conductivity up to about $10^5 \Omega^{-1} \text{cm}^{-1}$.⁷⁻⁹ This suggests that polymers of various acetylene derivatives are able to form charge-transfer complexes with electron acceptor, and further that there is the possibility of the complexes formed being highly conducting.

Since polyacetylene is insoluble in any solvent and is very susceptible to air oxidation, various substituted acetylenes (soluble and stable to air oxidation) are synthesized and characterized.¹⁰ Of these

polymers, poly(phenylacetylene) was extensively studied on its synthesis and electrical conductivity. However, there have been few reports on the electrical conductivity of polyacetylenes containing aromatic heterocycles such as thiophene, furan, and pyrroles.

In recent years, we have reported the polymerization of 2-ethynylthiophene¹¹ and 2-ethynylfuran¹² by W- and Mo-based catalysts, and the characterization of the resulting poly(2-ethynylthiophene) (P2ET) and poly(2-ethynylfuran) (P2EF).

The present article presents the studies on the electrical conductivity of P2ET and P2EF doped with electron acceptor dopants. Also, the comparison of doping behavior and electrical conductivity of poly(phenylacetylene) (PPA) containing no heteroatom will be discussed.

EXPERIMENTAL

P2ET

P2ET was prepared by the polymerization of 2-ethynylthiophene catalyzed by WCl_6 -*n*- Bu_4Sn (1 : 2).¹¹ The polymer yield and number-average molecular weight were 96% and 21,600, respectively. The polymer was brown powder and completely soluble in organic solvents. The P2ET having low molecular weight ($M_n = 2,200$) was prepared by the

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radical polymerization using azobisisobutyronitrile (AIBN) [monomer/AIBN mol ratio = 50] at 60°C for 24 h. This polymer was light yellow powder and completely soluble in organic solvents.

P2EF

The polymerization of 2-ethynylfuran was carried out by the same method as that of 2-ethynylthiophene. The catalyst system was WCl_6 -*n*- Bu_4Sn (1 : 4). The polymer yield and number-average molecular weight were 43% and 12,000, respectively. The P2EF was black and partially soluble (about 55%) in organic solvents.

PPA

The polymerization of phenylacetylene was also carried out by the same method described in ref. 13. The catalyst system was WCl_6 - Ph_4Sn (1 : 1). The polymer yield and number-average molecular weight were 80% and 11,200, respectively. The PPA was light yellow powder and completely soluble in organic solvents.

Pellet Preparation

Polymer powder was pressed into a compaction pellet in a KBr pellet press (about 1,500 psi). The sample thickness was subsequently measured with a micrometer. The thickness of sample pellets was ranged from 0.05–0.1 cm, depending on the amount of polymer initially placed in the press.

Doping Procedure

Polymer pellets were placed in a dynamic vacuum chamber for 1–2 h to remove traces of absorbed solvent and moisture. The materials were then transferred into a vacuum desiccator containing 2 g solid iodine (resublimed) in a glass dish. The desiccator was evacuated for at least 10 min and then sealed. The doping was carried out at 20°C. The doping content was controlled by varying the time of exposure. The bromine doping was done by exposing the polymer pellet to the vapor of bromine in a hermetically sealed desiccator at room temperature. In the case of $FeCl_3$ doping, the sample was immersed in a nitromethane solution of $FeCl_3$ (concentration = 1.0M) at room temperature. The amount of dopants was estimated from the weight uptake method.¹⁴

Measurements of Electrical Conductivity

The electrical conductivity of the sample polymer was determined using a standard four-point probe measurement.^{15–17} The electrical conductivity is given by the following formula:

$$\sigma = \frac{1}{2\pi S} \frac{I}{V},$$

where σ is the electrical conductivity ($\Omega^{-1} \text{ cm}^{-1}$), S is the distance between each probe, and I and V are the current and the voltage, respectively.

Instruments

The electrical conductivity of samples was measured with a Hewlett Packard 3490 multimeter and Keithley 616 Digital Electrometer. Infrared spectra were taken on a Perkin–Elmer Model 283 grating spectrometer using a potassium bromide. UV-visible spectra were obtained with a Cary 17 spectrophotometer. Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere at a heating rate of 10°C/min up to 600°C with a Perkin–Elmer TGS-1 thermobalance. X-ray diffraction analyses were performed on a JEOL X-ray diffractometer with Cu-K α radiation at a scan speed of 4°/min. Electron paramagnetic resonance (EPR) were conducted by Varian E-line EPR spectrometer at a frequency of 9.5 GHz.

RESULTS AND DISCUSSION

Doping

To know the doping (charge-transfer complex formation) ability of polyacetylenes carrying aromatic heterocycles, the doping experiment of P2ET, P2EF, and PPA by iodine were carried out. The doped iodine contents (the mol ratio of iodine to monomeric unit) of P2ET, P2EF, and PPA according to the doping time are shown in Figure 1. The doping ability of the conjugated polymers having 2-thienyl substituents was greater than that of PPA having phenyl substituent. The doping ability of P2EF having 2-furyl substituents was similar to that of PPA. In the case of P2ET, the maximum doping content was finally 1.1. This may be explained as follows. The thienyl substituents have more vinyl character than phenyl substituents of PPA and also have sulfur atom further oxidizable. The doping

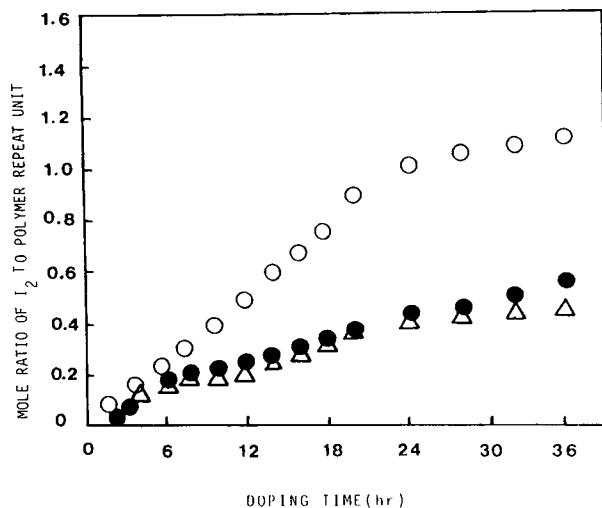


Figure 1 Doped iodine content of P2ET, P2EF, and PPA according to the doping time at 20°C; (○), P2ET; (●), P2EF; (△), PPA.

content of P2EF and PPA after doping for 36 h were finally 0.59 and 0.45, respectively.

Electrical Conductivity

Figure 2 shows the electrical conductivity of iodine-doped P2ET according to doped iodine content. The electrical conductivity increases from less than $10^{-10} \Omega^{-1} \text{cm}^{-1}$ for the undoped polymer to over $10^{-4} \Omega^{-1} \text{cm}^{-1}$ for iodine-doped polymer. The maximum conductivity of iodine-doped P2ET was $3 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$. The polymer color was changed from brown to shiny black.

Figure 3 shows the electrical conductivity of iodine-doped P2EF according to the doped iodine

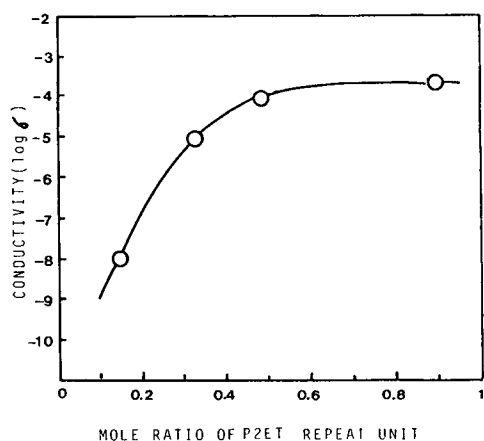


Figure 2 Electrical conductivity of P2ET doped with iodine according to the doped iodine content.

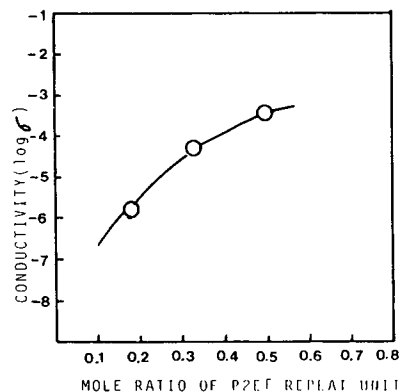


Figure 3 Electrical conductivity of P2EF doped with iodine according to the doped iodine content.

content as with P2ET. The electrical conductivity of P2EF by doping was increased to the value of $5 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$. The P2EF polymer color was changed from the original black to shiny black by doping.

The electrical conductivities of iodine-doped P2ET and P2EF show a systematic and large dependence on the iodine doping content, covering a range of six powers of ten, but reveal no discontinuous or abrupt changes that might be suggestive of a transition associated with the conduction mechanism. On the other hand, the electrical conductivity of iodine-doped PPA was in the range of $6 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$ and $1 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$.¹⁸

Table I shows the electrical conductivities of P2ET, P2EF, and PPA doped with various electron acceptor dopants except iodine. It was observed that the electrical conductivity of FeCl_3 -doped P2ET is the highest value ($1 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$) among the samples doped with various electron acceptor dopants. The electrical conductivities of Br_2 - and FeCl_3 -doped P2EF were $9.2 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ and $4.2 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$, respectively. On the other hand, the electrical conductivities of Br_2 - and AsF_5 -doped PPA were $2.0 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ and $1.1 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$, respectively. From these observations, we found that the electrical conductivity of a polyconjugated system containing aromatic heterocycles was higher than those of polyconjugated systems containing no heteroatom [i.e., PPA, poly(2-ethynyl-naphthylene), etc.].

Three samples of P2ET ($M_n = 2,200$, $M_n = 5,600$, $M_n = 21,600$) having different molecular weights were tested to find the molecular weight effect on the electrical conduction. The electrical conductivities of these three samples after doping with iodine were in the range of $2.0 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$ and 3.2

Table I Electrical Conductivity of P2ET, P2EF, and PPA Doped with Electron Acceptor Dopants

Polymer	Dopant	Composition of Doped Polymer	Electrical Conductivity ($\Omega^{-1} \text{ cm}^{-1}$)
P2ET	Br_2	$(\text{C}_6\text{H}_4\text{S})_1 (\text{Br}_2)_{0.1}$	1.8×10^{-5}
	FeCl_3	^a	1.0×10^{-3}
	$\text{BF}_3 \cdot \text{Et}_2\text{O}$	^a	2.7×10^{-6}
P2ET	Br_2	$(\text{C}_6\text{H}_4\text{C})_1 (\text{Br}_2)_{0.07}$	9.2×10^{-6}
	FeCl_3	^a	4.2×10^{-3}
PPA	Br_2	$(\text{C}_8\text{H}_6)_1 (\text{Br}_2)_{0.08}$	2.0×10^{-6}
	AsF_5	$(\text{C}_8\text{H}_6)_1 (\text{AsF}_5)_{0.6}$	1.1×10^{-4} ¹⁸

^a The doping content was not determined.

$\times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$ and the doped iodine contents were in the range of 0.81 and 0.94. The electrical conductivities of iodine-doped P2ET are nearly independent with increasing molecular weight of sample. This result is consistent with the results of polyacetylene¹⁹ and PPA.²⁰

Spectral Properties

The UV-visible spectrum of P2ET and iodine-doped P2ET was obtained in 1,2-dichloroethane as shown in Figure 4. The UV-visible spectrum of undoped P2ET show a broad absorption up to 600 nm, a characteristic peak of conjugated polymer. Upon iodine doping of P2ET, the intensity of the broad absorption was increased and extended over the entire UV-visible range of the spectrum to even 900 nm. The UV-visible spectrum of bromine-doped P2ET showed a similar spectral properties with iodine-doped P2ET.

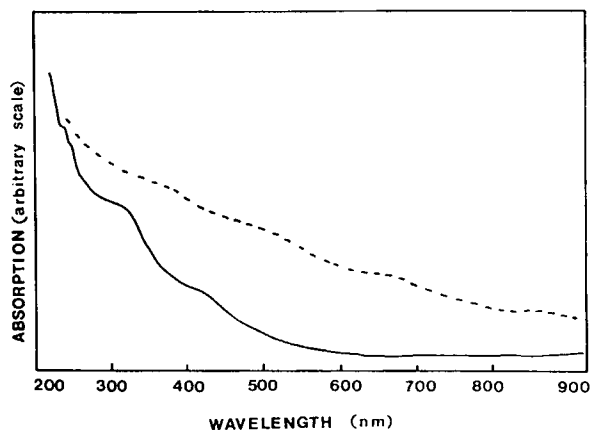


Figure 4 UV-visible spectra of P2ET (—) and iodine-doped P2ET (-----) in 1,2-dichloroethane.

Figure 5 shows the infrared spectra of P2ET and iodine-doped P2ET. The infrared spectrum of iodine-doped P2ET shows featureless absorption peaks. These features are originated from bond weakening resulting from electron transfer from polymer chain to the dopants.²¹⁻²³

The doping process also has been monitored by electron paramagnetic resonance (EPR). The line shape of the strong spin resonance in doped P2ET is distorted, a Dysonian line shape,²⁴ indicative of a high conductive sample. The line width (Hpp) of P2ET as a function of doped iodine content reveals narrowing of an initially broad signal, from 34 G at 2.0025 of *g* value to an intense and sharp signal, 14 G at 2.0059 of *g* value. The more localized free radicals in backbone could be selectively removed by dopant, resulting in decrease Hpp.

The thermal stability of P2ET and iodine-doped P2ET was tested as shown in Figure 6. The TGA

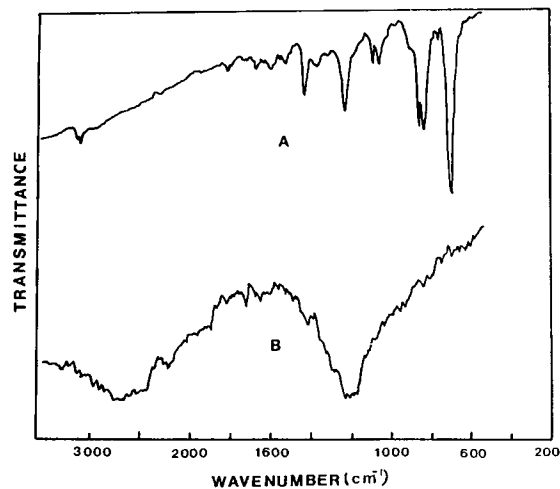


Figure 5 IR spectra of P2ET (A) and iodine doped P2ET (B) in EBr pellet.

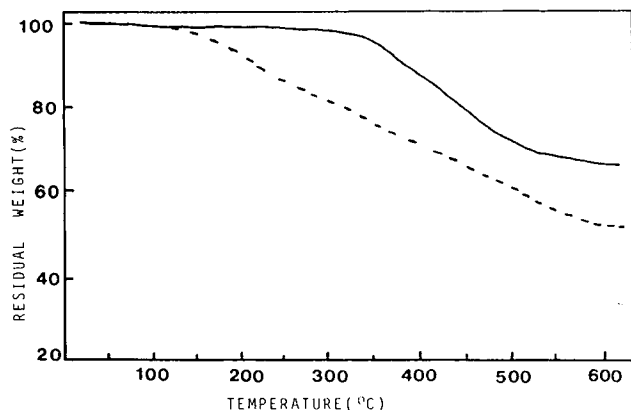


Figure 6 TGA thermograms of P2ET (—) and iodine-doped P2ET (-----).

thermogram of iodine-doped P2ET show that it retained 95% of its original weight at 180°C 90% at 225°C, and 53% at 600°C. The thermal stability of iodine-doped P2ET is more or less poorer than the undoped P2ET. This result can be explained by falling out of dopants because dopant-polymer interaction is reduced at a high-temperature region.

X-ray diffractograms of P2ET, P2EF, and doped P2ET and P2EF were obtained to know the crystallinity change according to doping. X-ray diffractograms of P2ET and P2EF showed a featureless broad peak. Also, the X-ray diffractograms of iodine-doped P2ET and P2EF showed a featureless broad peak. The ratios of half-height width to diffraction angle ($\Delta 2\theta/2\theta$) are all larger than 0.20. The value for amorphous polyethylene (0.28) is similar to these values, while those of crystalline polyethylene and cis-polyacetylene^{25,26} are much smaller. Therefore, it can be concluded that the present polymers irrespective of doping content are amorphous.

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