

COMMUNICATIONS TO THE EDITOR

Electrical Conductivity of Iodine-Doped Poly(dipropargyl ether) and Poly(dipropargyl sulfide)

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Conducting polymers have attracted considerable attention in the last few decades because their electrical conductivity can be increased in some cases by more than 12 orders of magnitude by doping, and these materials are applicable to solar energy cells, semiconductors, conductors, polymer batteries, etc.¹ Recently, various conjugated polymers were synthesized and characterized.² In 1983, Gibson reported the synthesis of the cyclic polyene, poly(1,6-heptadiyne), by the cyclopolymerization of 1,6-heptadiyne using Ziegler-Natta catalysts.³ The resulting polymer was obtained in the form of film and showed the highest electrical conductivity ($10^{-1} \sim 10^{-3} \Omega^{-1} \text{cm}^{-1}$) among substituted polyacetylenes.

In recent years, we have reported the cyclopolymerization of dipropargyl ether and dipropargyl sulfide by using the catalyst systems consisted with W- and Mo-based catalysts.⁴

The present communication reports the study on the electrical conductivity of iodine-doped poly(dipropargyl ether) [PDPE] and poly(dipropargyl sulfide) [PDPS].

The sample polymers were prepared as described in our previous paper.⁴ These polymers were easily oxidized in air to produce polymers containing carbonyl groups in the backbone. The PDPE is more susceptible to air oxidation than PDPS. Thus we used the sample polymer as soon as it was prepared. The sample pellets were formed by compression of the dried polymer powder in a KBr pellet press under 1500 psi pressure. The thickness of sample pellet was ranged from 0.05 cm to 0.15 cm, depending on the amount of polymer initially placed in the press.

Iodine doping was performed by exposing the polymer pellet to iodine vapor in the vacuum desiccator at 25 °C. The degree of doping (mole ratio of iodine to polymer repeating unit) was estimated from the weight uptake method.⁵ The doping ability of PDPS was greater than that of PDPE. Similar results were observed in the doping experiment of poly(2-ethynylthiophene) and poly(2-ethynylfuran) containing sulfur and oxygen atoms, respectively.⁷

The electrical conductivity of the sample was determined by using a standard four-point probe measurement without extensive pumping of the doped pellets. The distance of each probe, which was made from platinum, was 1 mm. Conductivity was calculated by the following equation.⁶

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

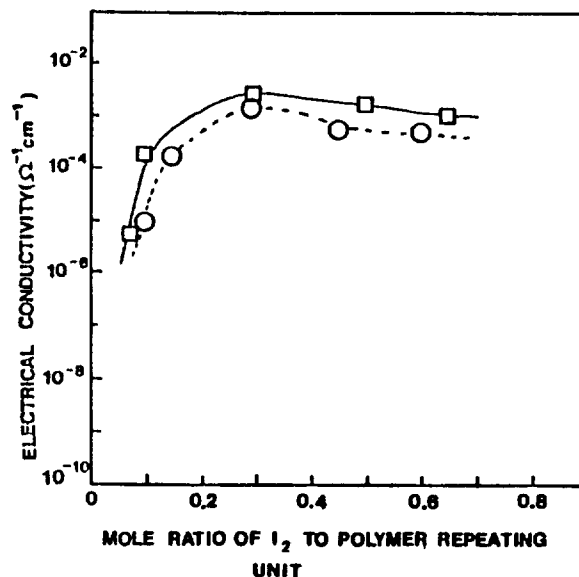


Figure 1. Electrical conductivity of iodine-doped poly(dipropargyl ether) [○] and poly(dipropargyl sulfide) [□].

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

Figure 1 shows the electrical conductivity of PDPE and PDPS according to the degree of doping of iodine. As the doping level increased, the electrical conductivity reached to a maximum value ($9.7 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ for PDPE, $3.2 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ for PDPS), and then decreased to a plateau at some lower level ($6 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$ for PDPE, $1 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ for PDPS). Similar trends were observed in the electrical conductivity study of iodine-doped poly(1,6-heptadiyne)³ and poly(dipropargylsilane)s.⁸

X-ray diffraction analyses were performed on JEOL X-ray diffractometer with Cu-K α radiation at a scan speed of 4°/min. Iodine-doped PDPE and PDPS display no crystallinity alike the undoped ones.

Figure 2 shows the infrared spectra of iodine-doped PDPE and PDPS in KBr pellet. The infrared spectra of doped polymers are more featureless than those of undoped polymers. The band weakening by doping is due to the elec-

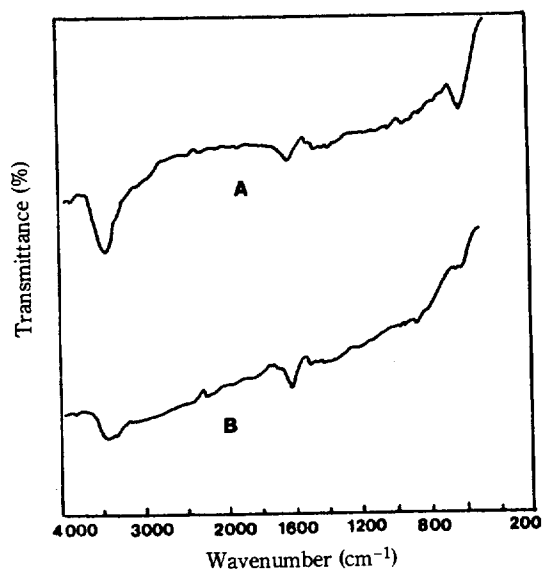


Figure 2. IR spectra of iodine-doped poly(dipropargyl Ether) [A, $(C_6H_6O)_1(I_2)_{0.30}$] and poly(dipropargyl sulfide) [B, $(C_6H_6S)_1(I_2)_{0.29}$]

tron transfer from polymer chain to the dopant.⁹ For iodine doped PDPE and PDPS, the infrared spectra show no C-I stretching bands in their normal region ($465-600\text{ cm}^{-1}$).¹⁰ This indicates that iodine atoms are not attached to carbon atoms by normal sigma bonds. This finding seems to be consistent with the results reported in the literature for bromine- and chlorine-doped poly(phenylacetylene).¹¹

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External NADH Oxidation of Mitochondrion Produces More Heat

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In the preface for the report¹ by one communicator of this communication, he stated that some people suffer a mild fever by the oral intake of ginseng roots. But he did not explain the cause of the fever broadly. It is supposed that a component of ginseng makes an organelle produce heat. Cold exposure in cold-adapted rats activated the pathway of external electron transport of mitochondrion for exogenous NADH oxidation² probably for heat production. This pathway donate its electron to the electron shuttle of cytochrome *c* in the intermembrane space of the organelle³⁻⁵. Because we could not find a report of measuring these heat production, we intended to measure the heat production or temperature elevation *in vitro* in the mitochondrial electron-transport systems (the ex-

ternal transport *via* cytochrome *c* and internal transport) and to compare them.

Mitochondria were separated from bovine heart by the method of Smith⁶ and quantitative analysis⁷ of the organelle was in terms of protein. The activity of the mitochondrion was determined in terms of absorption decrease of added NADH at 340 nm. The mitochondria were used by dispersing them in a isotonic buffer⁸-0.225M sucrose, 10 mM sodium phosphate, 5 mM $MgCl_2$, 20 mM KCl, 20 mM triethanolamine (pH 7.4). The final concentration of NADH in the reaction systems was $1.5 \times 10^{-4}M$.

Ginseng saponin was separated after Namba⁹ and its concentration in the reaction system was from 1.5×10^{-7}