Electro-optical and Electrochemical Properties of a Sulfur-Containing Polyacetylene

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1. INTRODUCTION

Conjugated organic polymers are of particular interest in material science because of their extraordinary optical and electronical properties. For more than several decades, electric conduction in organic solids has been one of the most fascinating topics for synthetic chemists and solid-state physics [1-3]. The initial impetus for the plethora of work on conducting polymers was generated by the discovery of the increase, by nearly 10 orders of magnitude, in the electrical conductivity in the oxidized form of π-conjugated polyacetylene (PA) [2].

Polymers having a conjugated backbone are expected to show unique properties, such as electrical conductivity, paramagnetism, migration and transfer of energy, color, chemical reactivity and complex formation ability [1]. Because of these properties, PA and its homologues have been promising as organic semiconductors, membranes for gas separation and for liquid-mixture separation, chiro-optical materials, side-chain liquid crystals, materials for chemical sensors, and materials for nonlinear optical properties as well as photo-luminescence and electroluminescence .

Generally, sulfur-containing polymers exhibit several unique properties, such as moderate hydrophilicity, complex-forming ability, and chemical reactivity in hydrolysis and oxidation. Although sulfur-containing polyacetylenes are expected to show interesting properties and functions based on their unique structure, only a few example of such polymers have been known so far, *e.g.,* poly(1-chloro-2-thienylacetylene), poly(2 or 3-ethynylthiophene), poly(dipropargyl sulfide), and poly(1-phenylthio-1-dodecyne).

Now, we report the electro-optical and electro-chemical properties of poly(phenyl propargyl sulfide) [poly(PPS)], a sulfur-containing polyacetylene derivative, prepared by transition metal catalysts.

2. EXPERIMENTAL

A typical synthetic procedure for poly(PPS) is as follows: Into a 25 mL reactor equipped with magnetic stirrer were sequentially added 1.0 g (6.75 mmol) of PPS, 39.8 mg (0.225 mmol, M/C = 30) of $PdCl_2$, and 10 mL of DMF ($[M]_0$ = 0.613 M). Then the polymerization was carried out at 90 $^\circ$C for 24 hrs under nitrogen atmosphere. The polymerization mostly proceeded in a homogeneous manner. The polymer solution was then diluted with 10 mL DMF and was precipitated into a large excess of methanol. The brown powder was obtained in 63% yield.

FT-IR spectra were obtained with a Bruker EQUINOX 55 spectrometer using a KBr pellet. NMR spectra were recorded on a Varian 500 MHz FT-NMR spectrometer (Model: Unity INOVA) in DMSO-d_6. The optical absorption spectra were measured by a Shimadzu UV-3100 UV-VIS-NIR spectrometer. The optical absorption spectra were measured by a HP 8453 UV-visible spectro-photometer. The photoluminescence spectra were obtained by Perkin Elmer luminescence spectrometer LS55 (Xenon flash tube) utilizing a lock-in amplifier system with a chopping frequency of 150 Hz. Electrochemical measurements were carried out with a Potentionstat/Galvanostat Model 273A (Princeton Applied Research). The electrochemical measurements were performed under 0.1 M tetrabutylammonium tetrafluoroborate solution containing acetonitrile. ITO, Ag/AgNO$_3$ and platinum wire were used as working, reference and counter electrode, respectively. X-ray diffractograms were obtained with a PHILLIPS X-ray diffractometer (Model: XPert-APD).

3. RESULTS AND DISCUSSION

The polymer yields for this polymerization by MoCl$_5$-Ph$_4$Sn and WCl$_6$-EtAlCl$_2$ catalyst systems

were 65% and 35%, respectively. In general, it was found that the catalytic activity of Mo-based catalysts was higher than that of W-based catalysts. PdCl$_2$ also polymerized PPS to give 63 % yield of polymer.

The polymer structure of poly(PPS) was characterized by NMR (^{1}H-, ^{13}C-), IR, and UV-visible spectroscopy, and elemental analysis. The elemental analysis data of reprecipitated poly(PPS) agreed well with the theoretical values: calcd for (C$_9$H$_8$S): C, 72.93%; H, 5.44%; S, 21.63%; found: C, 71.45%; H, 5.28 %; S, 20.97%.

The ^{1}H-NMR spectrum of poly(PPS) in DMSO-d$_6$ showed broadly the phenyl protons and the vinyl proton of the conjugated polymer backbone at 6.0-8.5 ppm. The characteristic methylene proton peaks were also observed at 3.4 ppm. The carbon peaks of phenyl substituent and vinyl carbons on the conjugated polymer backbone were observed in the region of 124-140 ppm.

The morphology of poly(PPS) was also investigated by X-ray diffraction analysis. Because the peaks in the diffraction pattern were broad and the ratio of the half-height width to diffraction angle ($\Delta 2\theta/2\theta$) was greater than 0.35 [1], the polymer was mostly amorphous. The number-average molecular weights of the polymers were in the range of 5,400-13,500.

The electro-optical and electrochemical properties of poly(PPS) were measured. Poly(PPS) showed the characteristic UV-visible absorption band at 360 nm and blue PL spectrum at 460 nm, corresponding to the photon energy of 2.70 eV. The energy band gap of poly(PPS) was estimated to be 2.77 eV from the analysis of the absorption edge with a plot of ($h\nu$) vs. ($\alpha h\nu$)^2, where α, h, and ν are absorbance, Planck's constant, and the frequency of light, respectively. We measured cyclic voltammograms of poly(PPS) with various scan rates (30 mV/s ~ 120 mV/s). The peak potentials are gradually shifted to higher potentials as the scan rate is increased. In addition, we have observed very stable cyclic voltammograms of poly(PPS) from the consecutive scan (up to 30 cycles), which means that this material has relatively stable redox process. The oxidation of poly(PPS) occurred at 0.25 V (*vs* Ag/AgNO$_3$), where the vinylene unit of the conjugated polymer backbone might be oxidized in the scan. Poly(PPS) also shows irreversible reduction at -1.45 V. The redox current value was gradually increased as the scan rate was increased. This result suggests that the electrochemical process of poly(PPS) is reproducible in the potential range of -1.75 ~ 0.70 V *vs* Ag/AgNO$_3$.

The oxidation current density of poly(PPS) *versus* the scan rate is an approximately linear relationship in the range of 30 mV/sec ~ 120 mV/sec. The exponent of the scan rate, the x value of poly(PPS), is found to be 0.577. This value means that the kinetics of the redox process is almost entirely controlled by the diffusion process.

4. CONCLUSIONS

Here, we synthesized a sulfur-containing polyacetylene, poly(PPS), by the polymerization of PPS by various transition metal catalysts. The polymer structure was characterized by various instrumental methods to have a conjugated polymer backbone system having the designed substituents. The cyclic voltammograms of the polymer exhibited reversible electrochemical behaviors between the doping and undoping peaks. It was found that the kinetics of the redox process of poly(PPS) was almost entirely controlled by the diffusion process, from the experiment plotting the oxidation current density of poly(PPS) *versus* the scan rate.

5. ACKNOWLEDGEMENT

6. REFERENCES

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