

Electrical Conductivity and Spectral Properties of Iodine-Doped Poly(2-ethynylpyridine)

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SYNOPSIS

This article includes the doping and dedoping behaviors, the electrical conductivity, and the spectral properties of poly(2-ethynylpyridine) and iodine-doped poly(2-ethynylpyridine). The doping ability of poly(2-ethynylpyridine) having a pyridine substituent was greater than that of polyphenylacetylene having a phenyl substituent. The electrical conductivity of iodine-doped poly(2-ethynylpyridine) increased with doping time and reached the value of about $5 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ when the mol ratio of iodine to poly(2-ethynylpyridine) repeating unit was above 0.7. The spectral properties of poly(2-ethynylpyridine) and iodine-doped poly(2-ethynylpyridine) were also studied by infrared and UV-visible spectroscopies and thermogravimetric analysis. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Conjugated polymers containing aromatic heterocycles such as thiophene, pyrrole, and furan have attracted considerable attention from a synthetic point of view and also due to their enhanced electrical conductivity.¹⁻⁷

Poly(2-vinylpyridine) is currently used as a cathode in pacemaker batteries in the form of its charge-transfer complex with iodine.⁸ Poly(2,5-pyridine) and poly(2,6-pyridinesulfide) were prepared and characterized.⁹⁻¹¹ Doping of these materials with iodine or ferric chloride increased its electrical conductivity from 1×10^{-14} to $1 \times 10^{-1} \Omega^{-1} \text{cm}^{-1}$.^{9,10}

In recent years, we reported the preparation and characterization of poly(2-ethynylpyridine) by various transition-metal catalysts.¹² The present article deals with the electrical and spectral properties of poly(2-ethynylpyridine) (P2EP) and iodine-doped poly(2-ethynylpyridine) and the comparison with that of a similar conjugated polymer, poly(phenylacetylene), having no heteroatom.

EXPERIMENTAL

Poly(2-ethynylpyridine) (P2EP)

P2EP was prepared as described elsewhere.¹² The catalyst for the polymerization was $\text{WCl}_6\text{-EtAlCl}_2$. The initial monomer concentration ($[M]_0$) and the EtAlCl_2 -to- WCl_6 mol ratio were 2M and 4, respectively. The resulting P2EP was a black powder and completely soluble in polar solvents such as lower alcohols and DMF, but insoluble in aromatic and halogenated hydrocarbons. The sample polymers used in the doping experiment were purified twice by reprecipitation from methanol solution into excess ethyl ether.

Pellet Preparation

P2EP powder was pressed into a compaction pellet in a KBr pellet press (about 1500 psi). The sample thickness was subsequently measured with a micrometer. The sample diameter and thickness were 13 and 0.5–0.7 mm, respectively. The density of the sample pellet was 1.41 g/cm^3 .

Doping Procedure

P2EP pellets were placed in a dynamic vacuum for 1–2 h to remove traces of absorbed solvent and

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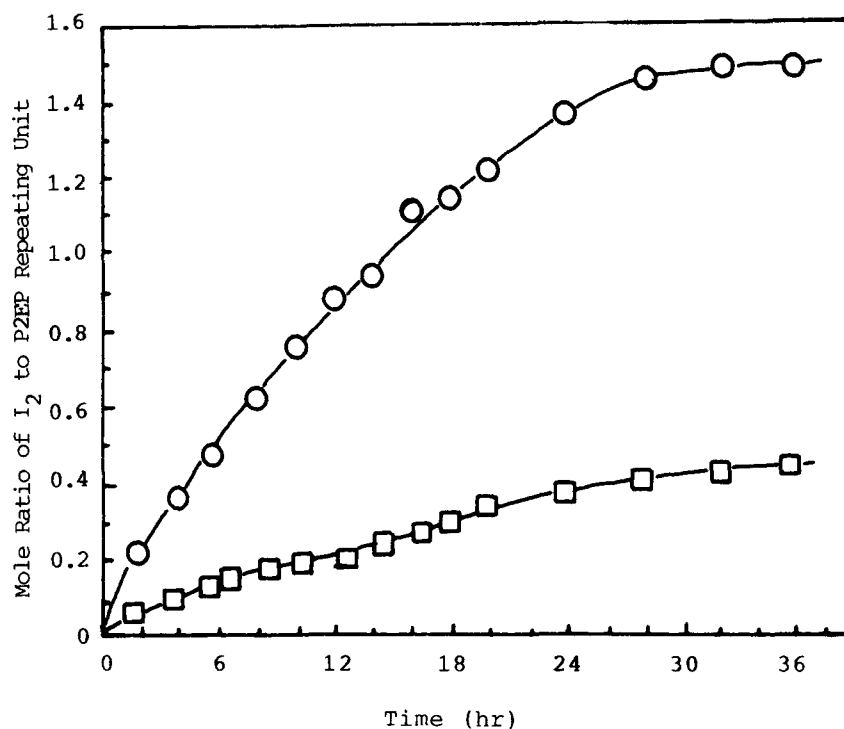


Figure 1 Doped iodine content of P2EP according to the doping time at 20°C: (○) P2EP; (□) poly(phenylacetylene).

moisture. The material was then transferred into a vacuum desiccator containing about 2 g of solid iodine (resublimed) in glass dish. The desiccator was evacuated for at least 10 min and then sealed. The sample was exposed to an iodine-saturated atmosphere at 20°C.

The doping level was controlled by varying the time of exposure. Upon iodine uptake, the original black-colored polymer turned into a shiny black color characteristic of charge-transfer complexes. The amount of iodine dopant was estimated from the weight uptake method.¹³

Measurement of Electrical Conductivity

The electrical conductivity of the sample was determined using a standard four-point probe technique.¹⁴⁻¹⁶ The distance of each probe, which was made from platinum, was 1 mm. The conductivity is given by the formula that follows:

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

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

Instruments

The electrical conductivity of the samples was measured with a Hewlett-Packard 3490 multimeter and a Keithley 616 Digital Electrometer. Infrared spectra of P2EP and iodine-doped P2EP were taken on a Perkin-Elmer 1600 series FTIR spectrometer using a potassium bromide. Thermogravimetric analyses (TGA) were performed under nitrogen atmosphere at a heating rate of 10°C/min up to 700°C with a Perkin-Elmer TGS-1 thermobalance. UV-visible spectra were obtained with a Carey 17 spectrophotometer in methanol.

RESULTS AND DISCUSSION

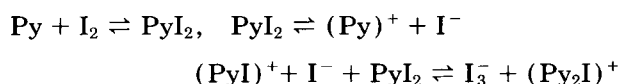
To understand the doping (charge-transfer complex formation) behaviors, P2EP pellets were doped by exposure to the iodine vapor. A similar homolog containing the phenyl substituent, the polyphenylacetylene[†] pellet was also doped under the same

[†] The polymerization of phenylacetylene was carried out by the $\text{WCl}_6\text{-Ph}_4\text{Sn}$ (1 : 1) catalyst system at 30°C for 1 h. Initial monomer concentration ($[M]_0$) and monomer-to-catalyst mol ratio were 1.0M and 100, respectively. The polymer yield (methanol-insoluble) and number-average molecular weight (\bar{M}_n) were 90% and 12,000, respectively.

conditions to compare the doping behavior of P2EP with that of polyphenylacetylene.

Figure 1 shows the doped iodine content of P2EP and polyphenylacetylene according to the doping time at 20°C. The doping ability of P2EP having a pyridine substituent was greater than that of polyphenylacetylene having a phenyl substituent. The final maximum doping level (the mol ratio of iodine to a monomeric unit of P2EP) was 1.532, whereas that of polyphenylacetylene was only 0.42 after doping for 36 h.

This high doping ability of P2EP can be explained as follows: The pyridine side group is basic, though electron-donating. The pyridine (Py) moiety has been suggested to react with iodine in polar solvents as follows¹⁷:



This suggests the possibility that there is another site for attack by iodine to produce *N*-iodopyridinium salts, as shown by¹⁸

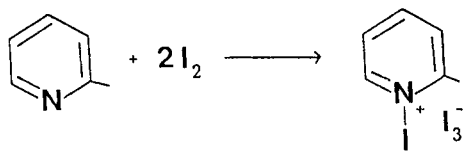


Figure 2 shows the dedoping (pumping) results of iodine-doped P2EP and polyphenylacetylene by continuous dynamic vacuum. The initial dedoping rate was very fast, but as the dedoping time was passed, the rate became very slow. Finally, the doping level was nearly constant after 20 h.

Undoped P2EP is an insulator and shows a conductivity less than $2.6 \times 10^{-12} \Omega^{-1} \text{cm}^{-1}$. Figure 3 shows the electrical conductivity of the P2EP pellet as a function of the mole ratio of iodine to the P2EP repeating unit. The electrical conductivity of iodine-doped P2EP at 20°C increases with time and reaches the value of about $5 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ when the mol ratio of iodine to P2EP is above 0.7. A similar trend was observed in the electrical conductivity of iodine-doped poly(3-thienylacetylene).¹⁹ The electrical conductivity of P2EP was higher than that of polyphenylacetylene by two orders of magnitude (the maximum electrical conductivity after doping with iodine was about $1 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$).²⁰

Figure 4 shows the infrared spectra of P2EP before and after iodine doping. The infrared spectrum of P2EP shows the aromatic C—H stretching band at 3049cm^{-1} , C=C and C=N stretching bands at $1619\text{--}1580 \text{cm}^{-1}$, and C—H out-of-plane deformation at 779cm^{-1} . Iodine doping induces more featureless broad peaks in most regions. This is due to the formation of a charge-transfer complex be-

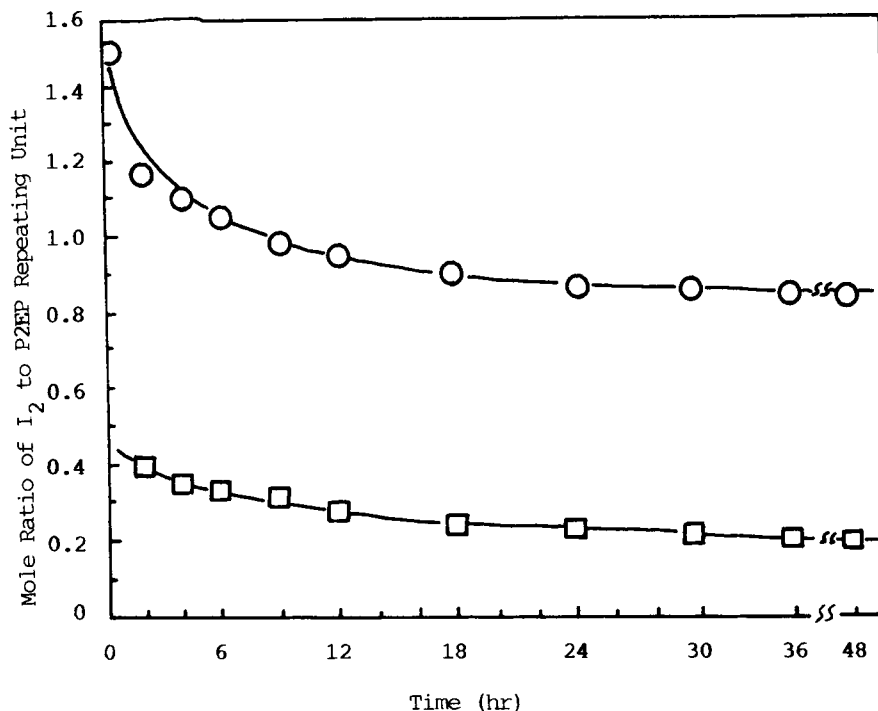


Figure 2 Doped iodine content of iodine-doped P2EP according to pumping time by continuous dynamic vacuum: (○) P2EP; (□) polyphenylacetylene.

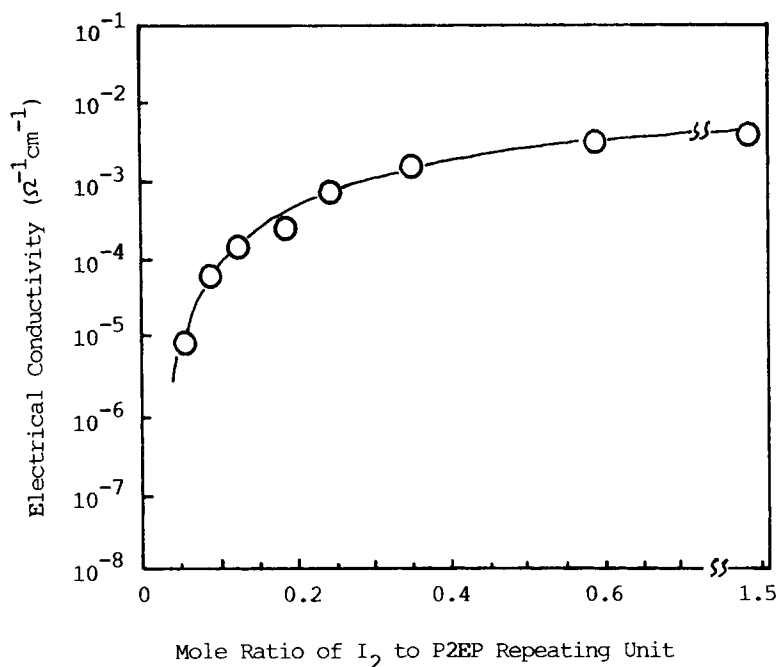


Figure 3 Electrical conductivity of iodine-doped P2EP.

tween polymer chain and iodine dopant. This was also verified by the absorption peak range shift from 1619, 1584, and 779 cm^{-1} to 1619, 1531, and 774 cm^{-1} , which was originated by C=C stretching, C=N stretching, and C—H out-of-plane deformation, respectively. For iodine-doped P2EP, the infrared spectra show no C—I stretching bands in their normal region (465–600 cm^{-1}).²¹ This indicates that iodine is not attached to carbon by normal sigma bonds. This finding seems to be consistent with the results reported in the literature for bromine and chlorine-doped polyphenylacetylene.²²

Figure 5 shows the absorption spectra of undoped and iodine-doped P2EP in methanol solution. The iodine-doped P2EP was slightly soluble, whereas the original (undoped) P2EP had been completely soluble in methanol, ethanol, DMF, etc. Despite drastic color changes in iodine-doped P2EP, the absorption spectrum of iodine-doped P2EP shows only broad, enhanced absorptions in the visible region (above 400 nm), not attributable to the polymer components.

Figure 6 shows the thermogravimetric analysis of P2EP and iodine-doped P2EP (the mol ratio of iodine to monomeric unit of P2EP: 0.7). The TGA thermogram of original P2EP shows that it retained 98% of its original weight at 100°C, 80% at 200°C, 44% at 400°C, and 26% at 700°C. However, the iodine-doped P2EP did not show an enhanced weight decrease even when the temperature increased up to 700°C. It retained 98% of its original weight at

200°C, 93% at 400°C, and 86% at 700°C. This indicates that the iodine intercalated P2EP was cross-linked when the doping proceeded and/or that the temperature was increased under nitrogen atmosphere during the TGA experiment. As with these results, the high content of charlike materials remained even after 700°C.

CONCLUSIONS

From this work, the following conclusions were obtained: First, the doping ability of P2EP carrying the pyridine substituent was greater than that of the polyphenylacetylene carrying the phenyl substituent. Second, the maximum electrical conductivity of iodine-doped P2EP was $5 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ when the mol ratio of the iodine to the P2EP repeating unit was above 0.7. Third, the formation of the charge-transfer complex between the polymer component and iodine dopant was verified by the characteristic wavenumber (e.g., 1619, 1584, and 779 cm^{-1}) shift to a lower wavenumber as the doping is performed. Fourth, the UV-visible spectra of iodine-doped P2EP show broad and enhanced absorptions at 400–700 nm not attributable to the polymer components. Lastly, in the TGA experiments, the iodine-doped P2EP did not show an enhanced weight loss even after 700°C. This indicated that the present iodine-doped P2EP was somewhat cross-linked when it is doped and/or the temperature is increased

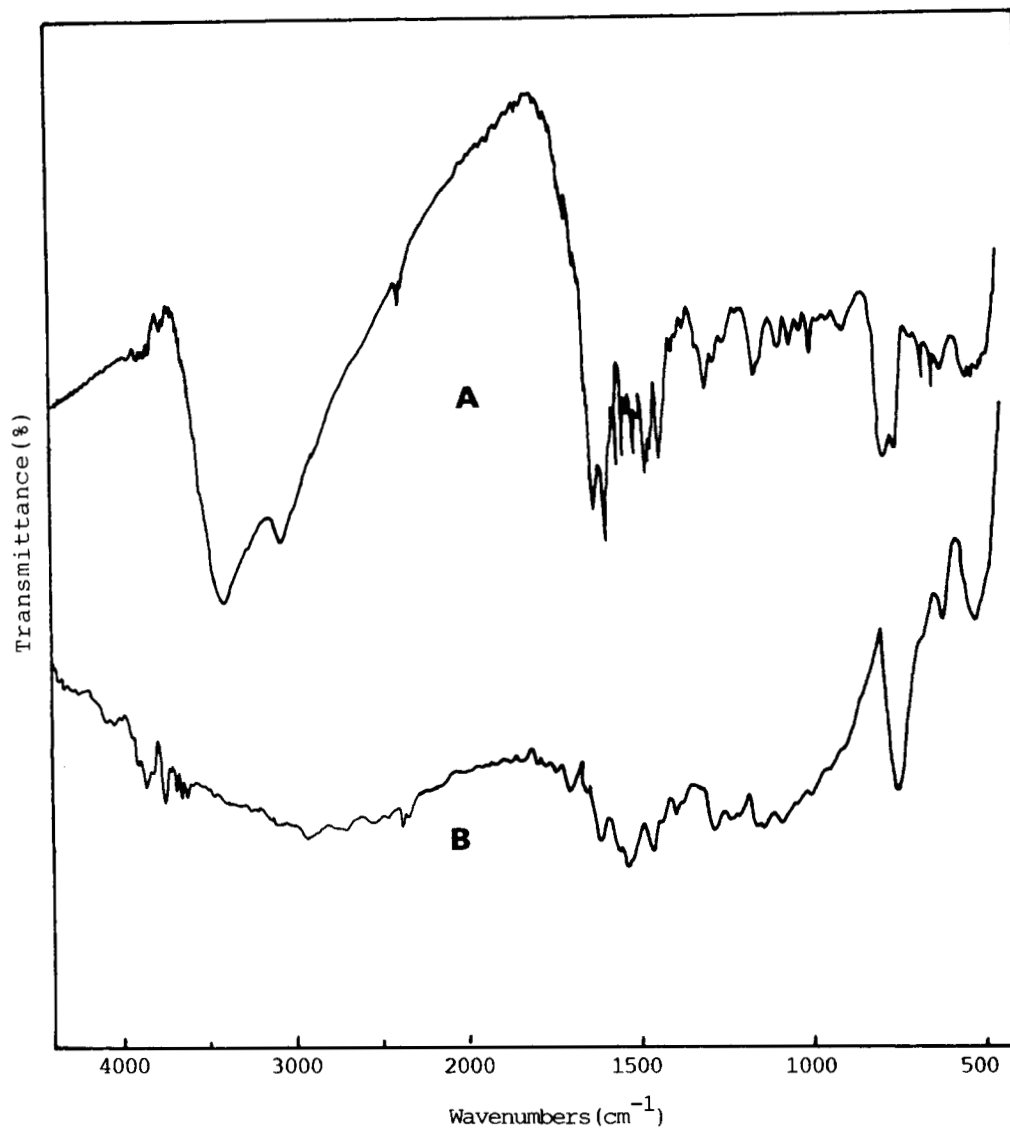


Figure 4 Infrared spectra of (A) P2EP and (B) iodine-doped P2EP.

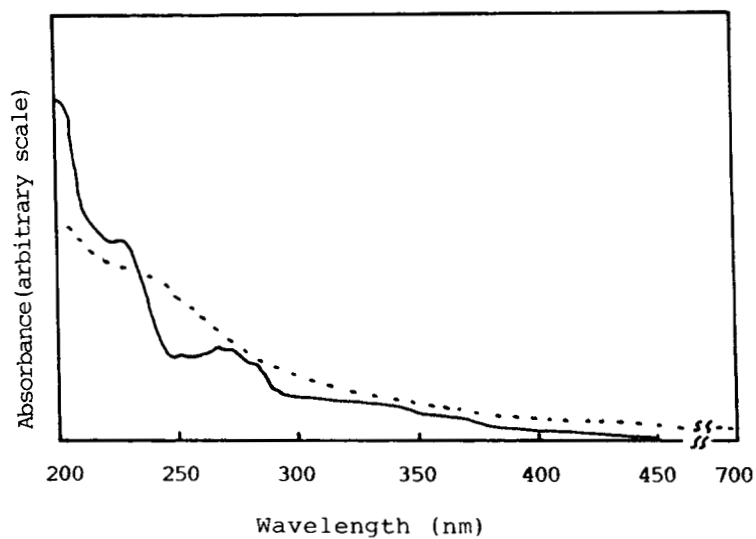


Figure 5 UV-visible spectra of (—) P2EP and (-----) iodine-doped P2EP in methanol solution.

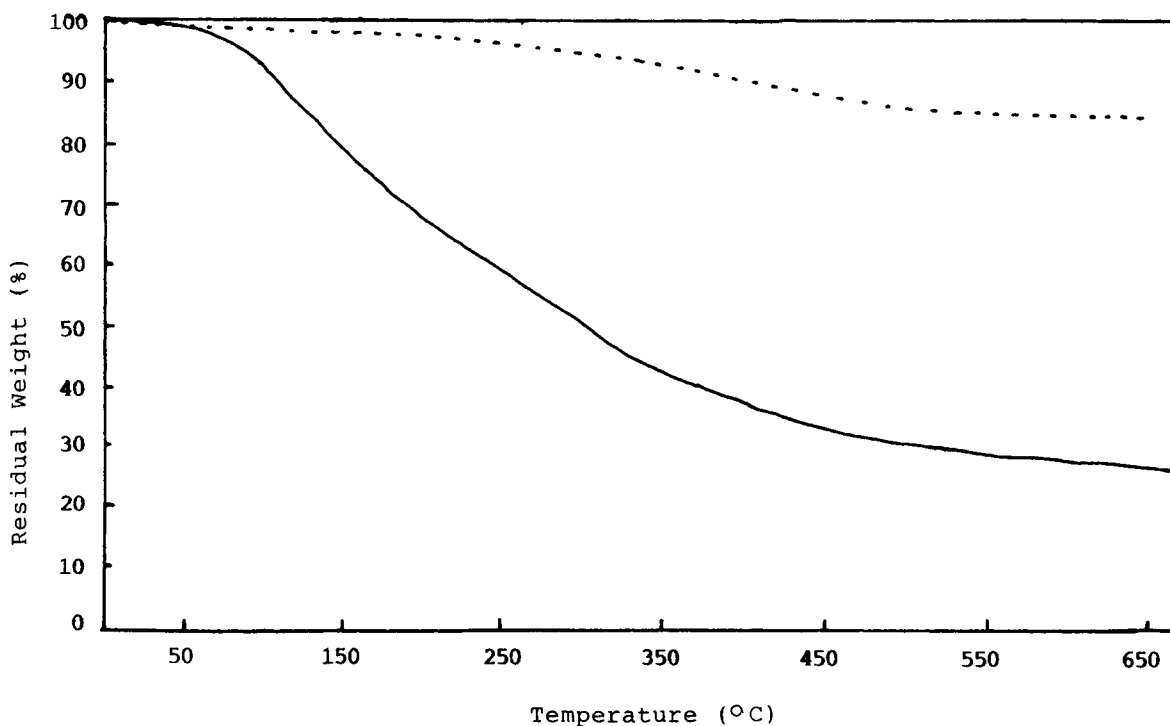


Figure 6 Thermogravimetric analyses of (—) P2EP and (-----) iodine-doped P2EP.

during the TGA experiment under nitrogen atmosphere.

REFERENCES

- R. H. Baughman, J. L. Bredas, R. R. Chance, R. L. Elsenbaumer, and L. W. Shacklette, *Chem. Rev.*, **82**, 209 (1982).
- A. J. Heeger, *Polym. J.*, **17**, 201 (1985).
- H. S. O. Chan, H. S. Munra, C. Davies, and E. T. Kang, *Synth. Met.*, **22**, 365 (1988).
- J. L. Bredas and A. J. Heeger, *Macromolecules*, **23**, 1150 (1990).
- H. L. Wang, L. Poppare, and J. E. Fernandez, *Macromolecules*, **23**, 1053 (1990).
- K. G. Neoh, E. T. Kang, S. H. Khor, and K. L. Tan, *J. Polym. Sci. Polym. Chem. Ed.*, **27**, 4365 (1989).
- N. V. Bhat and E. Sundaresan, *J. Appl. Polym. Sci.*, **38**, 1173 (1989).
- J. R. Ellis, in *Handbook of Conducting Polymers*, T. A. Skotheim, Ed., Marcell Dekker, New York, 1986, Vol. 1, p. 489.
- J. Laakso, J. E. Osterholm, and J. J. Lindberg, *Polym. Bull.*, **18**, 195 (1987).
- T. Yamamoto, T. Ito, K. Sanechika, and M. Hishimura, *Synth. Met.*, **25**, 103 (1988).
- G. Schiavon, G. Zotti, G. Bontempelli, and F. L. Loco, *Synth. Met.*, **25**, 365 (1988).
- Y. S. Gal, H. N. Cho, S. K. Kwon, and S. K. Choi, *Polymer (Korea)*, **12**, 30 (1988).
- C. K. Chiang, Y. W. Park, and A. J. Heeger, *J. Chem. Phys.*, **69**, 5098 (1978).
- R. L. Elsenbaumer and L. W. Shacklette, in *Handbook of Conducting Polymers*, T. A. Skotheim, Ed., Marcell Dekker, New York, 1986, Vol. 1, p. 224.
- E. T. Kang, E. J. Chung, and S. S. Im, *J. Appl. Polym. Sci.*, **33**, 317 (1987).
- Y. K. Lee and S. M. Jang, *Polymer (Korea)*, **10**, 125 (1986).
- H. Sasaki, T. Matsuyama, Y. Maeda, and H. Yamaka, *J. Chem. Phys.*, **75**, 5155 (1981).
- G. M. Phillips and D. R. Underaker, in *Proceedings of the Symposium on Lithium Batteries*, H. V. Benkatassetty, Ed., The Electrochemical Society, Minneapolis, MN, 1981.
- S. Tanaka, K. Okuhara, and K. Kaeriyama, *Makromol. Chem.*, **187**, 2793 (1986).
- P. Cukor, J. I. Krugler, and M. F. Rubner, *Makromol. Chem.*, **182**, 165 (1981).
- J. B. Lambert, H. F. Siurvell, L. Vebit, R. G. Cooks, and G. H. Stout, *Organic Structural Analysis*, Macmillan, New York, 1976, p. 247.
- P. S. Woon and M. F. Farona, *J. Polym. Sci. Polym. Lett. Ed.*, **13**, 567 (1975).

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