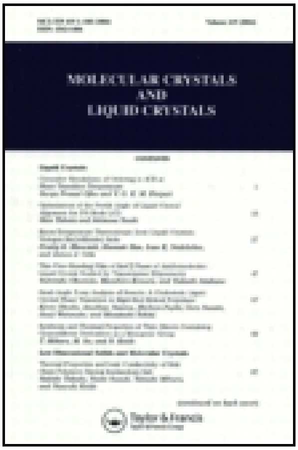

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Iodine Induced Polymerization and Oxidation of Pyridazine

E. T. Kang [a] , K. G. Neoh [a] , T. C. Tan [a] & H. C. Ti [a]
[a] Department of Chemical Engineering, National University of Singapore, Kent Ridge, Singapore, 0511

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Iodine Induced Polymerization and Oxidation of Pyridazine

E. T. KANG, K. G. NEOH, T. C. TAN and H. C. TI

Department of Chemical Engineering, National University of Singapore, Kent Ridge, Singapore 0511

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Simultaneous chemical polymerization and oxidation of pyridazine have been initiated by halogenic electron acceptor, iodine (I_2) in acetonitrile at and below room temperature. The polypyridazine-I_2 complex is granular in nature and has a room temperature d.c. electrical conductivity (σ) of about 2 $\text{ohm}^{-1}\ \text{cm}^{-1}$. A plot of $\ln \sigma$ vs. $(\text{temperature})^{-1/4}$ gives a straight line over the 120–300 K region. The physicochemical and thermal properties of the polypyridazine-I_2 complex are examined in detail. Bromine fails to produce a stable and conductive polymeric complex under the same experimental conditions.

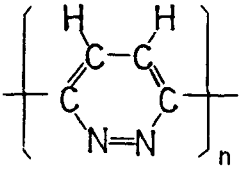
Keywords: polymerization and oxidation, pyridazine, electroactive, conductivity

INTRODUCTION

Electrically conductive conjugated polymers have been under intensive investigation in recent years.[1] Electrochemical polymerization and oxidation of conducting polyheterocycles with five-membered rings, such as polypyrrole,[2] polythiophene,[3] polyfuran[4] and polyselenophene[5] have become a common practice. More recently, conducting polyheterocycles with six-membered rings, such as polypyridazine,[6] have also been prepared by electrochemical method. In contrast to most of the chemically oxidized acetylene and phenylene polymers, polyheterocyclic cations prepared by the electrochemical method remain relatively stable when exposed to ambient conditions.[7] The availability of stable conductive polyheterocycles from electrochemical polymerization has encouraged us to search for alternative chemical methods of synthesis and oxidation for this family of polymers.

We reported recently on the simultaneous chemical polymerization and oxidation of pyrrole by halogens in aqueous media and in organic solvents.[8] The polypyrrole-halogen charge transfer (CT) complexes so produced are stable in the atmosphere and have electrical conductivities and conduction behaviour comparable to that of electrochemically prepared polypyrroles.[9] Thus, it becomes of great interest to extend the chemical synthesis and oxidation procedures to six-membered heterocycles, such as pyridazine.

The synthesis of semiconductive pyridazine-halogen compounds has been reported in a number of earlier studies.[10–12] The presence of pyridazine polymeric structures in these compounds has been suggested.[10,11] IR spectra of pyridazines and polypyridazine derivatives have also been studied with respect to interactions with side chains.[13] A recent study[6] suggested the following molecular structure for the electrochemically prepared polypyridazine:



In this communication, we report on the chemical polymerization and oxidation of pyridazine in acetonitrile and in the presence of iodine. The physicochemical properties of the resulting polypyridazine-I_2 complex are characterized by uv-visible and infrared (IR) absorption spectroscopy, thermogravimetric analysis (TGA), chemical analysis and electrical conductivity measurements.

EXPERIMENTAL

Polymer synthesis and oxidation

Pyridazine was obtained from Aldrich Chemical Co. and was purified by vacuum distillation. All solvents were of reagent grade and were The current passed varied from 1 to 10 mA. Conductivities below nitrogen atmosphere. The polymerization reactions were carried out either at room temperature (27°C) or at 0°C. About 2 g of solid iodine (sublimed, Aldrich Chemical Co.) was dissolved in about 125 ml of acetonitrile. Pyridazine (1 ml) was then introduced into the acetonitrile solution with vigorous stirring. The reaction mixture was stirred continuously for about 3–4 hours. During the process of stirring, black powdery precipitate began to appear in the solution. The black precipitate, which was later identified to be the polypyridazine-I_2 charge transfer complex, was removed by filtration and rinsed thoroughly with copious amounts of cold acetonitrile, carbon tetrachloride and absolute ethanol. The washing procedure was repeated until no unreacted monomer or acceptor could be detected in the ethanol wash by uv-visible absorption spectroscopy. The black precipitate was then dried by pumping under reduced pressure of 10^{-2} Torr for about 6 hours. The yield was about 50%, based on the amount of pyridazine species present in the complex.

Polymer characterization

The uv-visible absorption spectra were measured using a Shimadzu UV-260 spectrophotometer equipped with microprocessor. The IR absorption spectra measurements were carried out on a Perkin-Elmer Model 682 spectrophotometer with the polymer samples dispersed in KBr pellets. The chemical composition of the polymeric complexes were determined by elemental analysis. For electrical conductivity measurements, the polymer samples were pressed into thin circular discs of about 0.05–0.1 cm thick and 1.2 cm in diameter in a stainless steel press at a pressure of about 300 kg cm^{-2}. Electrical conductivities were measured using the standard collinear four-probe technique. The measuring circuit consisted of a Keithley 614 digital electrometer and a Hewlett-Packard Model 6212B d.c. power supply. The current passed varied from 1 to 10 mA. Conductivities below room temperature were measured *in situ* in a liquid nitrogen cryostat and in the presence of an inert atmosphere. Thermogravimetric analysis (TGA) were carried out using a Netzsch simultaneous TG-DTA apparatus, Model STA 409 at a heating rate of 10°C/min both in nitrogen and in air.

RESULTS AND DISCUSSION

Uv-visible and infrared absorption spectra

The polypyridazine-iodine complex prepared by the present method of polymerization and oxidation in acetonitrile is black in colour and granular in nature. The uv-visible absorption spectra of this iodine

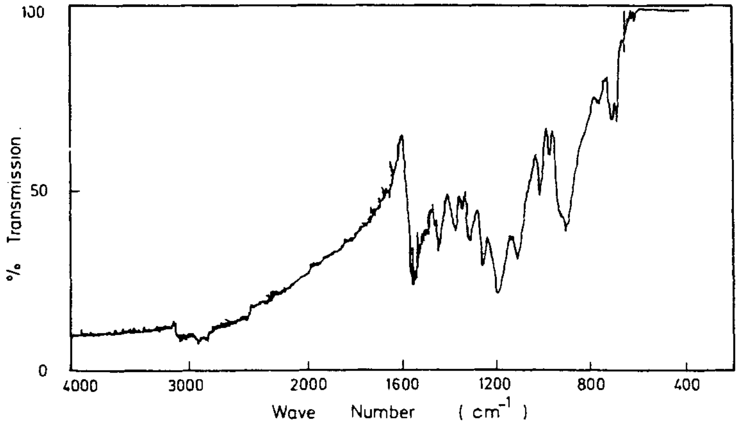


FIGURE 1 Infrared absorption spectra of chemically synthesized polypyridazine-I_2 CT complex.

complex is comparable, in general, with that of the oxidized polypyridazine, such as polypyridazine-ClO_4 complex, prepared by electrochemical method.[6] However, the spectra of the pyridazine-I_2 complex reveal an even broader absorption band in the red and an absorption tail extending well into the near-IR region. The red and near-IR absorption is probably associated with the charge transfer (CT) interaction between the conjugated polymer chain and the acceptor, since neutral polypyridazine has a band edge at about 1.8 eV.[6]

Figure 1 shows the IR absorption spectra of the polypyridazine-I_2 CT complex. The IR spectra reveal a rather featureless decrease in absorption from 4000 to 1700 cm^{-1}. This long absorption tail probably resulted from the tail of the absorption band located in the red and near-IR region. An IR absorption tail of similar nature has also been reported for chemically[8] as well as electrochemically[14] oxidized polypyrrole and has been associated with electrical conductivity in highly conducting polypyrroles. The region below 1700 cm^{-1} contains bands associated with the pyridazine moiety. The C—H aromatic stretching mode absorption at about 3100 cm^{-1} and the aliphatic mode at about 2840 and 2920 cm^{-1} are obscured by the absorption tail and are only barely visible. The aromatic C—H bending absorptions are, however, visible below 900 cm^{-1}. The presence of aliphatic C—H absorptions is consistent with the excess hydrogen in the chemical analysis (see Table I).

TABLE I

Chemical composition and electrical conductivity of the polypyridazine-I_2 complex

Sample no.	System	Polymerization condition	Chemical composition (normalized to C=4.0)	Conductivity (S cm^{-1}), 27°C
1	Polypyridazine-I_2	CH_3CN, 27°C	$C_{4.0}H_{2.9}N_{2.0}(I_2)_{0.66}$	2
2	Polypyridazine-I_2	CH_3CN, 0°C	$C_{4.0}H_{2.9}N_{2.0}(I_2)_{0.69}$	3
3	Polypyridazine-I_2 (compensated)*	CH_3CN, 0°C	$C_{4.0}H_{1.7}N_{2.0}(I_2)_{0.08}(NH_3)_{0.60}$	$< 10^{-8}$

*Obtained by exposure of Sample 2 to 5M NH_4OH solution for about 15 min.

Chemical compositions and electrical properties

Results of the elemental analysis of various polypyridazine-I_2 samples and their respective room temperature electrical conductivities are summarized in Table I. The data indicate that the CT complexes are primarily polymerized pyridazine units plus the halogen dopant. The present elemental analyses account for more than 96% of the materials in all samples. The lack of complete closure in the analyses indicates that the polypyridazine-I_2 complex may have been doped to a small extent by oxygen, as in the case of chemically[8,15] and electrochemically[14] oxidized polypyrrole.

There is no significant difference between the sample synthesized at room temperature and that at 0°C, as far as chemical compositions and electrical conductivities are concerned. The ratio of about three pyridazine units to two iodine molecules appears to represent the stable, optimum stoichiometric composition for the complex. Exhaustive extraction of Samples 1 and 2 with organic solvents, followed by vigorous pumping does not appear to cause any significant change in the monomer : acceptor ratio. The exact nature of the halogen anion remains to be determined by Raman spectroscopy.

The H mole ratio in the polypyridazine-I_2 complex is substantially above the theoretical value of two for a long linear chain of 3,6-disubstituted pyridazine rings.[6] Relative to this ideal structure, the excess hydrogen in the present complex readily indicates that some of the pyridazine rings may have been hydrogenated. Evidence for aliphatic as well as aromatic CH in the present complex is provided by the IR absorption spectra. The presence of partially saturated cyclic units has also been reported for electrochemically[14] as well as chemically[15] synthesized polypyrrole.

Treatment of the polypyridazine-I_2 CT complex with concentrated (5M) NH_4OH solution for about 15 minutes returns the polymer to an insulating state. The sample undergoes a change in color from black to dark brown, but remains insoluble in most organic solvents. Results of the chemical analysis on a carefully dried sample (Sample 3, Table I) suggest an almost complete removal of the halogen acceptor and a substantial addition of the ammonia species to the polymer. The IR absorption spectra of the NH_4OH treated complex reveal a complete disappearance of the absorption tail between 4000 to 1700 cm^{-1} and the appearance of strong N—H stretching and bending mode at about 3300–3500 cm^{-1} and 1610 cm^{-1}, respectively. The contribution of H_2O in NH_4OH to these absorption bands is probably negligible since the chemical composition specified in Table I accounts for over 99% of the elements in this particular sample. Thus, treatment of polypridazine-I_2 complex with NH_4OH probably involves a significant degree of interaction between the polymeric cationic sites and the basic ammonia species. The nature of such interaction, however, may be somewhat different from that of other acceptor doped conjugated polymers, such as polyacetylene,[16] since only oxidized polyheterocycles are believed to be stable so far.

The room temperature electrical conductivity (σ) of the present polypyridazine-I_2 CT complex is about 2 S cm^{-1}. The value is comparable to that of oxidized polypyridazine prepared by electrochemical method.[6] The conductivity was measured as a function of temperature (T). Figure 2 shows a typical ln σ versus $T^{-1/4}$ plot of the polypyridazine-I_2 CT complex near and below room temperature obtained from the standard four probe conductivity measurements. An apparent linear fit of the experimental data was obtained for the complex throughout the temperature range from 120 K to 300 K. The $T^{-1/4}$ dependence of σ has also been widely observed in other oxidized polyheterocycles, such as polypyrrole,[17] and has been interpreted in terms of Mott's model[18] of variable range hopping between localized states near the Fermi surface. In view of the recently reported inadequacy of the ordinary four probe conductivity measurements in overcoming the interfibrillar, intergranular and intercrystallitic contact resistance of polymer samples with metallic conductivity,[19,20] the physical significance of the $T^{-1/4}$ dependence in the present complex should be interpreted with care. We have also measured the temperature dependence of the conductivity in our polypyridazine-I_2 complex using the voltage shorted compaction technique.[19,21] However, no metallic temperature dependence of conductivity was observed.

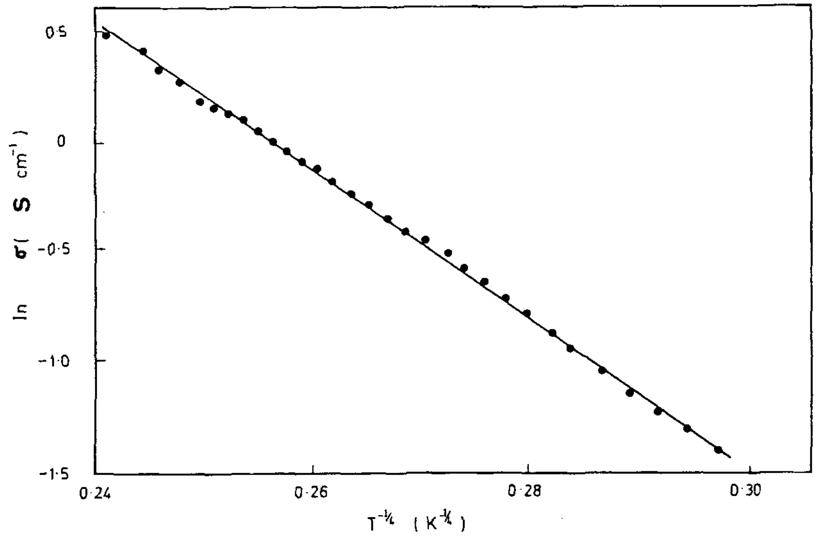


FIGURE 2 Temperature dependence of the electrical conductivity of polypyridazine-I_2 complex in four probe conductivity measurements.

Stability and thermal properties

Both the physicochemical and electrical properties of the present polypyridazine-I_2 complex show moderate stability in the atmosphere. The freshly prepared polypyridazine-I_2 complex is insoluble in most organic solvents. On standing in air for a period of about two weeks, the conductivity of most samples decreases by about one order of magnitude. Chemical analysis results show no significant change in the pyridazine : I_2 ratio. However, when the aged sample is dispersed in organic solvents, such as tetrahydrofuran, a yellow solution with black or dark brown precipitate results. Uv-visible absorption spectra measurement of the solution reveals the presence of iodine species only. These readily suggest that a free pyridazine polymeric structure must exist and that a progressive dissociation between the polymer and the acceptor must have occurred.

The thermogravimetric scans of the polypyridazine-I_2 CT complex in nitrogen and in air are shown in Figure 3. The polypyridazine-I_2 complex is stable to heating up to about 165°C in nitrogen and still retains about 25% of its original weight when heated to a temperature as high as 700°C. For scans carried out in air, the onset of major decomposition occurs at a slightly lower temperature and the sample loses all of its weight at about 650°C. It is interesting to note that the

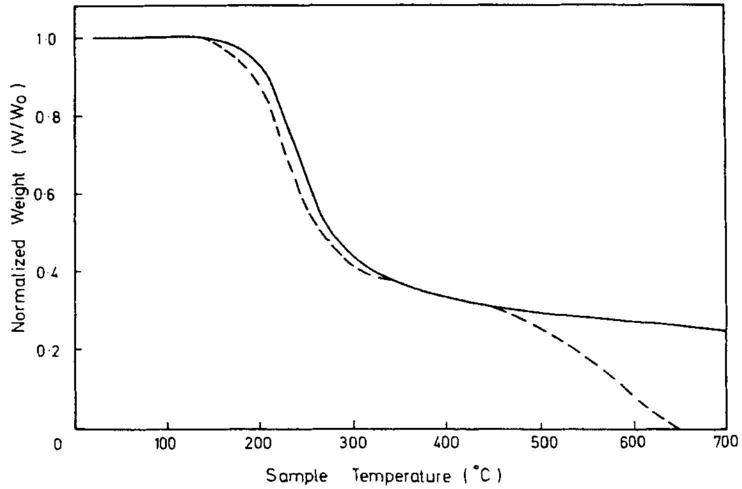


FIGURE 3 TGA scans of polypyridazine-I_2 complex in nitrogen (——) and in air (---).

weight loss in the present complex becomes rather rapid when heated slightly above the vaporization temperature of iodine (184°C). Furthermore, the initial rapid weight loss corresponds roughly to the amount of I_2 present in the complex. Thus, the initial thermal decomposition process incurred in the present polypyridazine-I_2 complex may be associated with the physical vaporization or removal of I_2 from the complex. A similar observation has been reported recently for the chemically synthesized polypyrrole-I_2 CT complex.[8]

Reactions with bromine

When a solution of bromine in acetonitrile was reacted with pyridazine under the same experimental conditions as that used in the synthesis of polypyridazine-I_2 complex, a dark brown precipitate was obtained. The dark brown solid has a conductivity in the order of 10^{-4} ohm^{-1} cm^{-1}. However, the complex degrades rapidly in air and becomes sticky and partially soluble in most organic solvents. Uv-visible absorption spectra measurements of the resulting solutions indicate the presence of the pyridazine species. Thus, the complex may not have involved an extensive degree of polymerization. Alternatively, a substantial degree of depolymerization may have occurred in the bromine complex.

CONCLUSION

A relatively simple method has been described for the simultaneous chemical polymerization and oxidation of pyridazine by iodine in acetonitrile. The polypyridazine-I_2 CT complex so produced is electroactive and has an electrical conductivity value comparable to that of electrochemically synthesized and oxidized polypyridazine.

Acknowledgments

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References

1. See for example, T. Skotheim, Editor, "*A Handbook on Conducting Polymers,*" Vols. I & II, Marcel Dekker, N.Y. (1985).
2. A. F. Diaz, K. Kanazawa and G. P. Gardine, *J. Chem. Soc. Chem. Commun.*, **635**, (1979).
3. R. J. Waltman, J. Bargon and A. F. Diaz, *J. Phys. Chem.*, **87**, 1459 (1983).
4. G. Tourillon and F. Garnier, *J. Electroanal. Chem.*, **135**, 173 (1982).
5. K. Yoshino, K. Kaneto, S. Inoue and K. Tsudagoshi, *Japan J. Appl. Phys.*, **22**, L701 (1983).
6. M. Satoh, K. Kaneto and K. Yoshino, *Japan J. Appl. Phys.*, **23**, L875 (1984).
7. F. Gutmann, H. Keyzer and L. E. Lyons, "*Organic Semiconductors, Part B,*" p. 207, R. E. Krieger Pub. Co., Florida (1983).

8a. E. T. Kang, T. C. Tan, K. G. Neoh and Y. K. Ong, *Polymer* (In press).

8b. E. T. Kang, K. G. Neoh, T. C. Tan and Y. K. Ong, *J. Macromol. Sci., Chem.* (In press).

9. E. T. Kang, K. G. Neoh and H. C. Ti, *Solid State Commun.*, **60**, 457 (1986).
10. R. J. Hoare and J. M. Pratt, *JCS Chem. Commun.*, **1320** (1969).
11. R. Drather and P. Laszlo, *JCS Chem. Commun.*, **180** (1970).
12. J. I. Hoppe and B. R. T. Keene, *JCS Chem. Commun.*, **188** (1970).
13. I. Gabe, E. Mantaluta and G. Neamtu, *Rev. Roum. Chim.*, **14**, 1163 (1969).
14. G. B. Street, T. C. Clarke, M. Krounbi, K. Kanazawa, V. Lee, P. Pfuger, J. C. Scott and G. Weiser, *Mol. Cryst. Liq. Cryst.*, **83**, 253 (1981).
15. M. Salmon, K. K. Kanazawa, A. F. Diaz and M. Krounbi, *J. Polym. Sci., Polym. Lett. Ed.*, **20**, 187 (1982).
16. T. C. Clarke and G. B. Street, *Synth. Met.*, **1**, 119 (1979/80).
17. A. Watanabe, M. Tanaka and J. Tanaka, *Bull. Chem. Soc. Jpn.*, **54**, 2278 (1981).
18. N. F. Mott and E. A. Davis, "*Electronic Process in Non-crystalline Materials,*" 2nd. Ed., p. 34, Clarendon Press, Oxford, (1979).
19. M. Wan, P. Wang, Y. Cao, R. Quan, F. Wang, X. Zhao and Z. Gong, *Solid State Commun.*, **47**, 759 (1983).
20. X. Bi, Y. Yao, M. Wan, P. Wang, K. Xiao, Q. Yang and R. Qian, *Makromol. Chem.*, **186**, 1101 (1985).
21. L. B. Coleman, *Rev. Sci. Instr.*, **49**, 58 (1978).